(54)[Title of the present invention] RECORDING MATERIAL,
SILVER HALIDE PHOTOGRAPHIC PHOTOSENSITIVE MATERIAL,
PHOTOTHERMOGRAPHIC MATERIAL, THERMALLY DEVELOPABLE IMAGE
FORMING METHOD, THERMALLY SENSITIVE RECORDING MATERIAL,
THERMALLY SENSITIVE RECORDING IMAGE FORMING METHOD AND INFRARED
RAY ABSORBING COMPOSITION WHICH EACH CONTAIN NOVEL SQUARYLIUM
COMPOUND AND NOVEL SQUARYLIUM COMPOUND

## (57)[Abstract]

[Problem] An object of the present invention is to provide a recording material, a silver halide photographic photosensitive material, a photothermographic material and a thermally developable image forming method which each contain a novel squarylium compound as a dye and, further, a thermally sensitive recording material containing the novel squarylium compound as a dye for thermal conversion and a thermally sensitive recording image forming method using the thermally sensitive recording material and, still further, an infrared ray absorbing composition containing the novel squarylium compound as a dye and, even still further, the novel squarylium compound.

[Means for Resolution] There is provided a recording material which is characterized by containing a squarylium compound represented by the general formula (1), (2) or (3) as described

below.[In the general formula (1), at least one of  $A^1$  and  $A^2$  represents a 5- or 6-membered nitrogen-containing heteroaromatic ring; in the general formula (2), at least one of  $A^3$  and  $A^4$  represents a 6-membered nitrogen-containing heteroaromatic ring represented by the general formula (2') as described below; and, in the general formula (3), at least one of  $A^5$  and  $A^6$  represents a quinoline ring or an isoquinoline ring.]

[Chemical 1]
general formula (1):

[Chemical 2]
general formula (2):

[Chemical 3]
general formula (2'):

$$Z^{1}$$
 $Z^{0}$ 
 $Z^{0$ 

[Chemical 4]
general formula (3):

[Claims]

[Claim 1] A recording material, being characterized by comprising a squarylium compound represented by the following general formula (1), (2) or (3):

[Chemical 1]

general formula (1):

in the general formula (1), at least one of A<sup>1</sup> and A<sup>2</sup> represents a 5- or 6-membered nitrogen-containing heteroaromatic ring; [Chemical 2] general formula (2):

in the general formula (2), at least one of A<sup>3</sup> and A<sup>4</sup> represents a 6-membered nitrogen-containing heteroaromatic ring represented by the following general formula (2'):

[Chemical 3]

general formula (2'):

$$Z_{n}^{1}$$
  $Z_{n}^{2}$   $Z_{n}^{2}$   $Z_{n}^{2}$   $Z_{n}^{2}$   $Z_{n}^{2}$   $Z_{n}^{2}$   $Z_{n}^{2}$ 

in the general formula 2',  $R^1$  and  $R^2$  each represent a hydrogen atom, -OR4 or -NR5R6; R4 represents a group substitutable to a hydrogen atom or an oxygen atom; R<sup>5</sup> and R<sup>6</sup> each represent a group substitutable to a hydrogen atom or a nitrogen atom; a ring may be formed containing R<sup>1</sup> and R<sup>2</sup> in a same ring; R<sup>5</sup> and  $R^6$  may be bonded to form a 5- or 6-membered ring;  $Z^1$  to  $Z^6$  each represent a carbon atom or a nitrogen atom in which at least one of  $Z^1$  to  $Z^6$  represents a nitrogen atom and at least one of the rest represents a carbon atom; at least one of carbon atoms represented by Z<sup>1</sup> to Z<sup>6</sup> is bonded with a squarylium carbon in the general formula (2); R<sup>3</sup> represents a substituent bondable atom forming a 6-membered nitrogen-containing heteroaromatic ring represented by the general formula (2'); and n represents an integer of 0 to 4; and [Chemical 4]

general formula (3):

in the general formula (3), at least one of  $A^5$  and  $A^6$  represents a quinoline ring or an isoquinoline ring.

A silver halide photographic photosensitive [Claim 2]

material, being characterized by comprising the squarylium compound as represented by the above-described general formula (1).

[Claim 3] A silver halide photographic photosensitive material, being characterized by comprising the squarylium compound as represented by the above-described general formula (2).

[Claim 4] A silver halide photographic photosensitive material, being characterized by comprising the squarylium compound as represented by the above-described general formula (3).

[Claim 5] A photothermographic material, being characterized by comprising the squarylium compound as represented by the above-described general formula (1), (2) or (3).

[Claim 6] Athermally developable image forming method, being characterized by exposing the photothermographic material as set forth in Claim 5 by using infrared laser light.

[Claim 7] A thermally sensitive recording material comprising the squarylium compound as represented by the above-described general formula (1), (2) or (3).

[Claim 8] A thermally sensitive recording image forming method, being characterized by exposing the thermally sensitive recording material as set forth in Claim 7 by using infrared laser light.

[Claim 9] An infrared ray absorbing composition, being characterized by comprising the squarylium compound as represented by the above-described general formula (1), (2) or (3).

[Claim 10] The squarylium compound as represented by the above-described general formula (1).

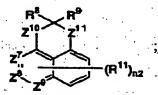
[Claim 11] The squarylium compound as represented by the above-described general formula (2).

[Claim 12] The squarylium compound as represented by the above-described general formula (3).

[Claim 13] A compound as represented by the following general formula (4):

[Chemical 5]

general formula (4):



in the formula,  $Z^7$  to  $Z^9$  each represent a carbon atom or a nitrogen atom; any one of  $Z^7$  to  $Z^9$  represents a nitrogen atom and the remaining two Z's are carbon atoms;  $Z^{10}$  represents an oxygen atom or  $NR^7$ ;  $Z^{11}$  represents an oxygen atom or  $NR^{10}$ ;  $R^7$  to  $R^{10}$  each represent a hydrogen atom, an alkyl group, a cycloalkyl group, a heterocyclic group or an aralkyl group;  $R^7$  and  $R^8$ ,  $R^8$  and  $R^9$ , and  $R^9$  and  $R^{10}$  may be bonded with each other in each combination to form a 5- or 6-membered ring;  $R^{11}$  represents a substituent

bondable to a quinoline ring or an isoquinoline ring; and n represents an integer of from 0 to 4.

[Detailed Description of the present invention]

[Technical Field to which the present invention Belongs]

The present invention relates to a recording material, a silver halide photographic photosensitive material, a photothermographic material, a thermally developable image forming method, a thermally sensitive recording material, a thermally sensitive recording image forming method and an infrared ray absorbing composition which each comprise a novel squarylium compound, and the novel squarylium compound.

# [Prior Art]

Although many of naphthalene squarylium dyes in which naphthalene derivatives are allowed to be materials have conventionally been known in, for example, J. Chem. Soc. Commun. pp. 452 to 454 (1993), and pyridine squarylium dyes have been known in publications, for example, Rocz. Chem., 44, 691 (1970), a squarylium dye in which a benzene condensed cyclic compound of a 6-membered nitrogen-containing heteroaromatic ring such as quinoline or isoquinoline is allowed to be a material has not been known.

[0003]

Further, many recording materials each using a ph enyl

squarylium dye, the naphthalene squarylium dye or the like have been proposed, a recording material using 5 - or 6-membered nitrogen-containing heteroaromatic ring is directly bonded with a squarylium ring has not been known at all and, accordingly, characteristics thereof have not been known.

[0004]

On the other hand, various types of compounds have been known each as an anti-halation and anti-irradiation dye of the silver halide photographic photosensitive material (inclusive of thermally developable material). Particularly, the anti-halation and anti-irradiation dye which has absorption in an infrared region of a spectrum is necessary for the silver halide photographic photosensitive material (inclusive of photothermographic material) recording material as a sensitized to an infrared wavelength, for example, that capable of performing recording by using an output of a near -infrared Although dihydroperimidine dye is used in USP No. 5,380,635, there was a problem in that sharpness was deteriora ted when a laser of 780 nm was used. Further, when it was used in a printing photosensitive material, it has been found that it exhibited a large absorbance in from 350 to 450 nm. Still further, although a dihydroperimidine squarylium dye was used in JP-A No. 10-016410 as a dye for photothermal conversion, it has been found that there was a problem in a residual ratio of a dye.

[0005]

[Problems that the present invention is to Solve]

An object of the present invention is to provide a recording material, a silver halide photographic photosensitive material, a photothermographic material and a thermally developable image forming method which each comprise a novel squarylium compound as a dye and, further, a thermally sensitive recording material comprising the novel squarylium compound as a dye for thermal conversion and a thermally sensitive recording image forming method using the thermally sensitive recording material and, still further, an infrared ray absorbing composition comprising the novel squarylium compound as a dye and, even still further, the novel squarylium compound.

[0006]

[Means for Solving the Problems]

The above-described object has been attained by constitutions as described below.

[0007]

1. A recording material, being characterized by comprising a squarylium compound represented by the following general formula (1), (2) or (3).

[8000]

[Chemical 6]

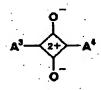
general formula (1):

[0009]

[In the general formula (1), at least one of A 1 and A2 represents a 5- or 6-membered nitrogen-containing heteroaromatic ring.]
[0010]

[Chemical 7]

general formula (2):



[0011]

[In the general formula (2), at least one of  $A^3$  and  $A^4$  represents a 6-membered nitrogen-containing heteroaromatic ring represented by the following general formula (2').

[.0012]

[Chemical 8]

general formula (2'):

$$Z^{1}$$
 $Z^{2}$ 
 $Z^{3}$ 
 $Z^{4}$ 
 $Z^{4}$ 
 $Z^{5}$ 
 $Z^{6}$ 
 $Z^{7}$ 
 $Z^{7$ 

[0013]

(in the general formula (2'),  $R^1$  and  $R^2$  each represent a hydrogen atom,  $-OR^4$  or  $-NR^5R^6$ ;  $R^4$  represents a group substitutable to

a hydrogen atom or an oxygen atom;  $R^5$  and  $R^6$  each represent a group substitutable to a hydrogen atom or a nitrogen atom; a ring may be formed containing  $R^1$  and  $R^2$  in a same ring;  $R^5$  and  $R^6$  may be bonded to form a 5- or 6-membered ring;  $Z^1$  to  $Z^6$  each represent a carbon atom or a nitrogen atom in which at least one of  $Z^1$  to  $Z^6$  represents a nitrogen atom and at least one of the rest represents a carbon atom; at least one of carbon atoms represented by  $Z^1$  to  $Z^6$  is bonded with a squarylium carbon in the general formula (2);  $R^3$  represents a substituent bondable to an atom forming a 6-membered nitrogen-containing heteroaromatic ring represented by the general formula (2'); and  $n^1$  represents an integer of 0 to 4.)]

[0014]

[Chemical 9]

general formula (3):

[0015]

[In the general formula (3), at least one of  $A^5$  and  $A^6$  represents a quinoline ring or an isoquinoline ring.]

2. A silver halide photographic photosensitive material, being characterized by comprising the squarylium compound as represented by the above-described general formula (1).
[0016]

- 3. A silver halide photographic photosensitive material, being characterized by comprising the squarylium compound as represented by the above-described general formula (2).
  [0017]
- 4. A silver halide photographic photosensitive material, being characterized by comprising the squarylium compound as represented by the above-described general formula (3).
  [0018]
- 5. A photothermographic material, being characterized by comprising the squarylium compound as represented by the above-described general formula (1), (2) or (3).
  [0019]
- 6. A thermally developable image forming method, being characterized by exposing the photothermographic material as set forth in Claim 5 by using infrared laser light.
  [0020]
- 7. A thermally sensitive recording material comprising the squarylium compound as represented by the above -described general formula (1), (2) or (3).
  [0021]
- 8. Athermally sensitive recording image forming method, being characterized by exposing the thermally sensitive recording material as set forth in Claim 7 by using infrared laser light.

[0022]

9. An infrared ray absorbing composition, being characterized by comprising the squarylium compound as represented by the above-described general formula (1), (2) or (3).

[0023]

10. The squarylium compound as represented by the above-described general formula (1).

11. The squarylium compound as represented by the above-described general formula (2).
[0025]

12. The squarylium compound as represented by the above-described general formula (3).
[0026]

13. A compound as represented by the following general formula (4).

[0027]

[Chemical 10]

general formula (4):

[0028]

[In the formula,  $Z^7$  to  $Z^9$  each represent a carbon atom or a nitrogen atom; any one of  $Z^7$  to  $Z^9$  represents a nitrogen atom and the

remaining two Z's are carbon atoms; Z<sup>10</sup> represents an oxygen atom or NR<sup>7</sup>; Z<sup>11</sup> represents an oxygen atom or NR<sup>10</sup>; R<sup>7</sup> to R<sup>10</sup> each represent a hydrogen atom, an alkyl group, a cycloalkyl group, a heterocyclic group or an aralkyl group; R<sup>7</sup> and R<sup>8</sup>, R<sup>8</sup> and R<sup>9</sup>, and R<sup>9</sup> and R<sup>10</sup> may be bonded with each other in each combination to form a 5- or 6-membered ring; R<sup>11</sup> represents a substituent bondable to a quinoline ring or an isoquinoline ring; and n<sup>2</sup> represents an integer of from 0 to 4.] Hereinafter, the present invention will be described in detail below.

The squarylium compound as represented by the general formula (1), (2) or (3) will be described.
[0030]

In the above-described general formula (1), at least one of A<sup>1</sup> and A<sup>2</sup> is a 5- or 6-membered nitrogen-containing heteroaromatic ring (for example, a pyrrole ring, a pyrazole ring, an imidazole ring, an oxazole ring, a thiazole ring, a triazole ring, an oxadiazole ring, a thiadiazole ring, an indole ring, a benzimidazole ring, a benzthiazole ring, a purine ring, a pyridine ring, a pyrazine ring, a pyrimidine ring, a pyrazine ring, a triazine ring, a quinoline ring, an isoquinoline ring, a purine ring, acinnoline ring, aquinoxaline ring or an acrydine ring) and, further, A<sup>3</sup> and A<sup>4</sup> as represented by the above-described general formula (2) are each preferably a 6-membered nitrogen-containing heteroaromatic ring as

represented by the general formula (2') and have each particularly preferably a constitution of a quinoline ring or an isoquinoline ring.

[0031]

In the general formula (2') in the above-described general formula (2),  $Z^1$  to  $Z^6$  each represent a carbon atom or a nitrogen atom and any one of  $Z^1$  to  $Z^6$  represents a nitrogen atom and at least one of the rest represents a carbon atom and, further, at least one of carbon atoms as represented by  $Z^1$  to  $Z^6$  is bonded with a squarylium carbon in the general formula (2).

R<sup>1</sup> and R<sup>2</sup> each represent a hydrogen atom, -OR<sup>4</sup> or -NR<sup>5</sup>R<sup>6</sup>. Further, a ring containing R<sup>1</sup> and R<sup>2</sup> in a same ring may be formed. Although R<sup>4</sup> represents a substituent substitutable to a hydrogen atom or an oxygen atom and R<sup>5</sup> and R<sup>6</sup> each represent a substituent substitutable to a hydrogen atom or a nitrogen atom, specific examples of such substituents each substitutable to an oxygen atom as represented by R<sup>4</sup> and those of such substituents each substitutable to a nitrogen atom as represented by R<sup>5</sup> and R<sup>6</sup> include halogen atoms (a chlorine atom, a bromine atom, an iodine atom, a fluorine atom and, of these atoms, preferably a bromine atom being mentioned), alkyl groups (each having preferably from 1 to 20 carbon atoms, more preferably from 1 to 12 carbon atoms and, particularly preferably, from 1 to 8 carbon atoms; for example, methyl, trifluoromethyl, ethyl, iso-propyl,

tert-butyl, n-octyl, n-decyl, n-hexadecyl, cyclopropyl, cyclopentyl and cyclohexyl groups being mentioned), alkenyl groups (each having preferably from 2 to 20 carbon atoms, more preferably from 2 to 12 carbon atoms and, particularly preferably, from 2 to 8 carbon atoms; for example, vinyl, allyl, 2 -butenyl and 3-pentenyl groups being mentioned), alk ynyl groups (each having preferably from 2 to 20 carbon atoms, more preferably from 2 to 12 carbon atoms and, particularly preferably, from 2 to 8 carbon atoms; for example, propargyl and 3 -pentynyl groups being mentioned), aryl groups (each having preferably from 6 to 30 carbon atoms, more preferably from 6 to 20 carbon atoms and, particularly preferably, from 6 to 12 carbon atoms; for example, phenyl, p-methyl phenyl and naphthyl groups being mentioned), amino groups (each having preferably from 0 to 20 carbon atoms, more preferably from 0 to 10 carbon atoms and, particularly preferably, from 0 to 6 carbon atoms; for example, amino, methyl amino, dimethyl amino, diethyl amino and dibenzyl amino groups being mentioned), acyl groups (each having preferably from 1 to 20 carbon atoms, more preferably from 1 to 16 carbon atoms and, particularly preferably, from 1 to 12 carbon atoms; for example, acetyl, benzoyl, formyl and pivaloyl groups being mentioned), alkoxycarbonyl groups (each having preferably from 2 to 20 carbon atoms, more preferably from 2 to 16 carbon atoms and, particularly preferably, from 2 to 12 carbon atoms; for example, methoxycarbonyl and ethoxycarbonyl

groups being mentioned), aryloxycarbonyl groups (each having preferably from 7 to 20 carbon atoms, more preferably from 7 to 16 carbon atoms and, particularly preferably, from 7 to 12 carbon atoms; for example, a phenyloxycarbonyl group being mentioned), acylamino groups (each having preferably from 2 to 20 carbon atoms, more preferably from 2 to 16 carbon atoms and, particularly preferably, from 2 to 10 carbon atoms; for example, acetylamino and benzoylamino groups being mentioned), alkoxycarbonylamino groups (each having preferably from 2 to 20 carbon atoms, more preferably from 2 to 16 carbon a toms and, particularly preferably, from 2 to 12 carbon atoms; for example, group being mentioned), methoxycarbonylamino aryloxycarbonylamino groups (each having preferably from 7 to 20 carbon atoms, more preferably from 7 to 16 carbon atoms and, particularly preferably, from 7 to 12 carbon atoms; for example, a phenyloxycarbonylamino group being mentioned), sulfonylamino groups (each having preferably from 1 to 20 carbon atoms, more preferably from 1 to 16 carbon atoms and, particularly preferably, from 1 to 12 carbon atoms; for example, methane sulfonylamino and benzene sulfonylamino groups being mentioned), sulfamoyl groups (each having preferably from 0 to 20 carbon atoms, more preferably from 0 to 16 carbon atoms and, particularly preferably, from 0 to 12 carbon atoms; for example, sulfamoyl, methyl sulfamoyl and dimethyl sulfamoyl groups being mentioned), carbamoyl groups (each having preferably from 1 to 20 carbon

atoms, more preferably from 1 to 16 carbon atoms and, particularly preferably, from 1 to 12 carbon atoms; for example, carbamoyl, methyl carbamoyl, diethyl carbamoyl and phenyl carbamoyl groups being mentioned), alkyl sulfonyl groups (each having preferably from 1 to 20 carbon atoms, more preferably from 1 to 16 carbon atoms and, particularly preferably, from 1 to 12 carbon atoms; for example, methyl sulfonyl and ethyl sulfonyl groups being mentioned), aryl sulfonyl groups (each having preferably from 6 to 20 carbon atoms, more preferably from 6 to 16 carbon atoms and, particularly preferably, from 6 to 12 carbon atoms; for example, a phenyl sulfonyl group being mentioned), sulfinyl groups (each having preferably from 1 to 20 carbon atoms, more preferably from 1 to 16 carbon atoms and, particularly preferably, from 1 to 12 carbon atoms; for exa mple, methane sulfinyl and benzene sulfinyl groups being mentioned), ureido groups (each having preferably from 1 to 20 carbon atoms, more preferably from 1 to 16 carbon atoms and, particularly preferably, from 1 to 12 carbon atoms; for example, ureido, methyl ureido and phenyl ureido groups being mentioned), hydroxyl groups, heterocyclic groups (for example, triazolyl, imidazolyl, pyridyl, furyl, piperidyl and morpholino groups being mentioned). These substituents may each be subjected to a further substitution.

R<sup>5</sup> is preferably a hydrogen atom.

[0033]

R<sup>4</sup> and R<sup>6</sup> are each preferably an alkyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group and, particularly preferably, an alkyl group.

[0034]

When a ring containing R<sup>1</sup> and R<sup>2</sup> in a same ring is formed, the ring is preferably a 6 or more-membered ring and, particularly preferably, a 6-membered ring.

[0035]

R<sup>3</sup> represents a substituent bondable to an atom forming 6-membered nitrogen-containing heteroaromatic ring as represented by the general formula (2') in the general formula (2) and specific examples of R3's include alkyl groups (each having preferably from 1 to 20 carbon atoms, more preferably from 1 to 12 carbon atoms and, particularly preferably, from 1 to 8 carbon atoms; for example, methyl, ethyl, iso-propyl, tert-butyl, n-octyl, n-decyl, n-hexadecyl, cyclopropyl, cyclopentyl and cyclohexyl groups being mentioned), alkenyl groups (each having preferably from 2 to 20 carbon atoms, more preferably from 2 to 12 carbon atoms and, particularly preferably, from 2 to 8 carbon atoms; for example, vinyl, allyl, 2 -butenyl and 3-pentenyl groups being mentioned), alkynyl groups (each having preferably from 2 to 20 carbon atoms, more preferably from 2 to 12 carbon atoms and, particularly preferably, from 2 to 8 carbon atoms; for example, propargyl and 3 -pentynyl groups being mentioned), aryl groups (each having preferably from 6

to 30 carbon atoms, more preferably from 6 to 20 carbon atoms and, particularly preferably, from 6 to 12 carbon atoms; for example, phenyl, p-methyl phenyl and naphthyl groups being mentioned), amino groups (each having preferably from 0 to 20 carbon atoms, more preferably from 0 to 10 carbon atoms and, particularly preferably, from 0 to 6 carbon atoms; for example, amino, methyl amino, dimethyl amino, diethyl amino and dibenzyl amino groups being mentioned), alkoxy groups (each having preferably from 1 to 20 carbon atoms, more preferably from 1 to 12 carbon atoms and, particularly preferably, from 1 to 8 carbon atoms; for example, methoxy, ethoxy and butoxy groups being mentioned), aryloxy groups (each having preferably from 6 to 20 carbon atoms, more preferably from 6 to 16 carbon atoms and, particularly preferably, from 6 to 12 carbon atoms; for example, phenyloxy and 2-naphthyloxy groups being mentioned), acyl groups (each having preferably from 1 to 20 carbon atoms, more preferably from 1 to 16 carbon atoms and, particularly preferably, from 1 to 12 carbon atoms; for example, acetyl, formyl and pivaloyl groups being mentioned), benzoyl, alkoxycarbonyl groups (each having preferably from 2 to 20 carbon atoms, more preferably from 2 to 16 carbon atoms and, particularly preferably, from 2 to 12 carbon atoms; for example, methoxycarbonyl and ethoxycarbonyl groups being mentioned), aryloxycarbonyl groups (each having preferably from 7 to 20 carbon atoms, more preferably from 7 to 16 carbon atoms and,

particularly preferably, from 7 to 12 carbon atoms; for example, a phenyloxycarbonyl group being mentioned), acyloxy groups (each having preferably from 2 to 20 carbon atoms, more preferably from 2 to 16 carbon atoms and, particularly preferably, from 2 to 10 carbon atoms; for example, acetoxy, benzoyloxy groups being mentioned), acylamino groups (each having preferably from 2 to 20 carbon atoms, more preferably from 2 to 16 carbon atoms and, particularly preferably, from 2 to 10 carbon atoms; for example, acetylamino and benzoylamino groups being mentioned), alkoxycarbonylamino groups (each having preferably from 2 to 20 carbon atoms, more preferably from 2 to 16 carbon atoms and, particularly preferably, from 2 to 12 carbon atoms; for example, a methoxycarbonylamino group being mentioned), aryloxycarbonylamino groups (each having preferably from 7 to 20 carbon atoms, more preferably from 7 to 16 carbon atoms and, particularly preferably, from 7 to 12 carbon atoms; for example, a phenyloxycarbonylamino group being mentioned), sulfonylamino groups (each having preferably from 1 to 20 carbon atoms, more preferably from 1 to 16 carbon atoms and, particularly preferably, from 1 to 12 carbon atoms; for example, methane sulfonylamino and benzene sulfonylamino groups being mentioned), sulfamoyl groups (each having preferably from 0 to 20 carbon atoms, more preferably from 0to 16 carbon atoms and, particularly preferably, from 0 to 12 carbon atoms; for example, sulfamoyl, methyl sulfamoyl and

dimethyl sulfamoyl groups being mentioned), carbamoyl groups (each having preferably from 1 to 20 carbon atoms, more preferably from 1 to 16 carbon atoms and, particularly preferably, from 1 to 12 carbon atoms; for example, carbamoyl, methyl carbamoyl, diethyl carbamoyl and phenyl carbamoyl groups being mentioned), alkylthio groups (each having preferably from 1 to 20 carbon atoms, more preferably from 1 to 16 carbon atoms and, particularly preferably, from 1 to 12 carbon atoms; for example, methylthio and ethylthio groups being mentioned), arylthio groups (each having preferably from 6 to 20 carbon atoms, more preferably from 6 to 16 carbon atoms and, particularly preferably, from 6 to 12 carbon atoms; for example, a phenylthio group being mentioned), sulfinyl groups (each having preferably from 1 to 20 carbon atoms, more preferably from 1 to 16 carbon atoms and, particularly preferably, from 1 to 12 carbon atoms; for example, methane sulfinyl and benzene sulfinyl groups being mentioned), ureido groups (each having preferably from 1 to 20 carbon atoms, more preferably from 1 to 16 carbon atoms and, particularly preferably, from 1 to 12 carbon atoms; for example, ureido, methyl ureido and phenyl ureido groups being mentioned), phosphoric amide groups (each having preferably from 1 to 20 carbon atoms, more preferably from 1 to 16 carbon atoms and, particularly preferably, from 1 to 12 carbon atoms; for example, diethyl phosphoric amide and phenyl phosphoric amide being mentioned), hydroxyl groups,

mercapto groups, halogen atoms (for example, florine, chlorine, bromine and iodine atoms), cyano groups, sulfo groups, carboxyl groups, nitro groups, hydroxamic groups, sulfino groups, hydrazino groups, heterocyclic groups (for example, imidazolyl, pyridyl, furyl, piperidyl and morpholino groups being mentioned). These substituents may each be subjected to a further substitution.

[0036]

 $n^1$  represents an integer of from 0 to 4 and preferably 0 or 1 and, particularly preferably, 0. [0037]

A bonding position of the squarylium ring is ordinarily an ortho-position or a para-position relative to  $R^1$  or  $R^2$ . [0038]

In the general formula (3), at least one of A 5 and A6 represents a quinoline ring or an isoquinoline ring.

A compound as represented by the general formula (4) will be described in detail.

In the above-described general formula (4),  $Z^7$  to  $Z^9$  each represent a carbon atom or a nitrogen atom and any one of  $Z^7$  to  $Z^9$  represents a nitrogen atom and the remaining two  $Z^7$  represent carbon atoms.  $Z^{10}$  represents an oxygen atom or NR $^7$  and  $Z^{11}$  represents an oxygen atom or NR $^{10}$ .  $n^2$  represents an

integer of from 0 to 4, preferably that of 0 or 1 and, p articularly preferably, that of 0.

[0041]

 $R^{11}$  represents a substituent bondable to a quinoline ring or an isoquinoline ring and, specifically, the examples as described in  $R^3$  in the general formula (2') in the general formula (2) are also preferable in  $R^{11}$ .

Alkyl groups as represented by R<sup>7</sup> to R<sup>10</sup> are such alkyl groups as each having from 1 to 20 carbon atoms and, preferably, from 1 to 12 carbon atoms (for example, methyl, ethyl, propyl, butyl, hexyl and undecyl groups). These alkyl groups may each be substituted by any one of halogen atoms (F, Cl and Br), alkoxycarbonyl groups (for example, methoxycarbonyl and ethoxycarbonyl groups), a hydroxyl group, alkoxy groups (for example, methoxy, ethoxy, phenoxy, isobutoxy groups), a sulfogroup (salt thereof being permissible), a carboxylic group (salt thereof being permissible) and acyloxy groups (for example, acetyloxy, butylyloxy, hexyloxy and benzoyloxy groups).

Examples of cycloalkyl groups as represented by R $^7$  to R $^{10}$  include cyclopentyl and cyclohexyl groups. [0044]

Aralkyl groups as represented by  $R^7$  to  $R^{10}$  are preferably such aralkyl groups as each having from 7 to 12 carbon atoms

(for example, benzyl and phenyl ethyl groups) and may each have any one of substituents (for example, methyl and methoxy groups and a chlorine atom).

Examples of heterocyclic groups as represented by R 7 to R 10 include a thienyl group, a furyl group, a pyrrolyl group, a pyrazolyl group, a pyridyl group and an indolyl group.

[0046]

 $R^7$  and  $R^{10}$  are each preferably a hydrogen atom. [0047]

 $R^7$  and  $R^8$ ,  $R^8$  and  $R^9$ , or  $R^9$  and  $R^{10}$  may be bonded with each other in each combination to form a cyclopentane or cyclohexane ring.

[0048]

[0045]

Specific examples of squarylium compounds (dyes) as represented by the general formula (1), (2) or (3) according to the present invention will be described below but the present invention is not limited thereto.

[0049]

[Chemical 11]

[0050]

[Chemical 12]

## 1-8

## 1-9

### 4 \_ 40

R;CH2OC(=0)C2H8

[0051]

[Chemical 13]

$$\begin{array}{c|c} C_2H_5 & HN & & \\ \hline \\ C_2H_5 & & \\ \hline \end{array} \begin{array}{c} O & & \\ O & & \\ \hline \end{array} \begin{array}{c} O & & \\ O & & \\ \hline \end{array} \begin{array}{c} NH & \\ C_2H_5 & \\ \hline \end{array} \begin{array}{c} C_2H_5 & \\ \hline \end{array}$$

# 1-13

#### 1-14

# 1-15

[0052]

[Chemical 14]

1 - 17

1-18

1-19

1-20

[0053]

[Chemical 15]

$$C^{4}H^{9}$$
 $N$ 
 $C^{4}H^{9}$ 
 $N$ 
 $C^{4}H^{9}$ 

### 1 - 23

#### 1 - 24

#### 1 - 25

[0054]

[Chemical 16]

$$1-28$$

$$(C_2H_5)_2N N(C_2H_5)_2O N(C_2H_5)_2 N(C_2H_6)_2$$

[0055]

[Chemical 17]

[0056]

Specific examples of compounds as represented by the general formula (4) according to the present invention will be described below but the present invention is not limited

thereto.

[0057]

[Chemical 18]

4-1

4-2

4-3

4-4

4-5

[0058]

[Chemical 19]

$$4-6$$

$$C_2H_5 \times C_2H_5$$

$$HN$$

$$4-7$$

$$4-8$$

$$HN$$

$$A-9$$

$$H_3C \times CH_5$$

$$N$$

$$A-10$$

[0059]

Examples of the recording materials according to the present invention include not only silver halide photosensitive materials such as a color negative film, a color reversal film, a color paper, a graphic art film and a medical X-ray film, photothermographic materials such as an output of a medical

laser imager and an output of a graphic art image setter, but also a recording material or printing plate in use of near-infrared light, particularly, a semiconductor laser, a direct printing plate, a photoresist material, optical recording materials such as an optical disc, an electrophotographic recording material, an inkjet recording material and a thermally-sensitive recording material.

The compound according to the present invention can be utilized in filter dyes for, for example, a band -pass filter, an optical filter and a thermal ray absorbing filter, ink for invisible printing, an infrared ray absorbing paint for anti-reflection of laser light, an electrophotographic toner, an toner, acceleration type thermally-fixing electrophotographic photoreceptor, sensitizer a · photopolymerization or photo-crosslinking, optical recording materials such as an optical disk, ink for inkjet, dyes for thermally-sensitive transfer, dyes for photothermal conversion, an infrared ray absorbing composition for use in an optical sensor and the like, silver halide photosensitive materials and the like.

[0061]

A spectral sensitizer, a silver halide emulsion and the like to be used in a silver halide photosensitive material in a case in which the compound according to the present invention

is used in the silver halide photosensitive material can be referred to JP-A No. 6-43583 and the like. [0062]

The compound according to the present invention can be used for a position detection of a silver halide photographic photosensitive material with reference to JP-A No. 09-96891 and the like.

[0063]

Further, the compound according to the present invention can be used in a photothermographic material with reference to methods as described in JP-A Nos. 10-114151 and 10-16410 and the like.

[0064]

The compound according to the present invention can be utilized in a filter, ink and paint with reference to JP -A Nos. 64-69686 and 58-1762.

[0065]

The photothermographic material according to the present invention is to form a photographic image by using a thermally developing process.

Photothermographic materials used for forming the photographic image, employing the thermally developing process, are disclosed, for example, in U.S. Pat. Nos. 3,152,904 and 3,457,075 and D. Morgan and B. Shely, "Thermally Processed Silver Systems" (Imaging Processes and Materials) Neblette, 8th

Edition, edited by Sturge, V. Walworth, and A. Shepp, page 2, 1969.

[0066]

The dye according to the present invention is preferably added after being dissolved in an organic solvent. The dye may be added in the range of from 0.1 to 1000 mg/m² and, preferably in the range of from 1 to 200 mg/m². When a binder is simultaneously used, the dye is in the range, based on the weight of the binder, of from 0.1 to 60% by weight, preferably of from 0.2 to 30% by weight and, more preferably, of from 0.5 to 10% by weight.

[0067]

The photothermographic material according to the present invention preferably has a photosensitive layer containing an organic silver salt, a binder and a photosensitive silver halide on a support. It is preferred that the dye of the invention contains in the photosensitive layer.

[8800]

A backing layer of the photosensitive material according to the present invention denotes a layer applied on the support at a side opposite to the photosensitive layer, and the dye according to the present invention is preferably contained in the backing layer.

[0069]

Examples of such supports capable of being applied to

the photothermographic material according to the present paper, a such as materials include invention polyethylene-coated paper, a polypropylene-coated paper, a parchment paper and cloth; sheets or thin films of metals such as aluminum, copper, magnesium and zinc; glass or glass coated with a metal such as chromium alloy, steel, silver, gold or platinum; synthetic polymer materials such as polyalkyl methacrylates (such as polymethylmethacrylate), polyesters (such as polyethyleneterephthalate), polyvinyl acetals, polyamides (such as nylon) and cellulose esters (such as cellulose nitrate, cellulose acetate, cellulose acetate propionate and cellulose acetate butyrate).

[0070]

In the photothermographic material according to the present invention, for example, a surfactant, an anti-oxidant, a stabilizer, a plasticizer, anultraviolet ray absorbing agent, a coating auxiliary and the like may be used.

[0071]

According to the present invention, an organic silver salt is a reducible silver source and a silver salt of an organic acid or a hetero-organic acid having a reducible silver ion source, specifically, a long chain (having from 10 to 30 carbon atoms and, preferably, from 15 to 25 carbon atoms) aliphatic carboxylic acid and a nitrogen-containing heterocylic ring are preferred.

An organic or inorganic silver salt complex is also useful in which a ligand has a total stability constant for silver ion of from 4 to 10. Examples of preferred silver salts are described in Research Disclosure, Items 17029 and 29963, and include the following; organic acid salts (for example, salts of gallic acid, oxalic acid, behenic acid, stearic acid, palmitic acid and lauric acid); carboxyalkylthiourea salts of silver 1-(3-carboxypropyl)thiourea (for example, 1-(3-carboxypropy1)-3,3-dimethylthiourea); silver complexes reaction products of aldehyde s of hydroxy-substituted aromatic carboxylic acids (for example, aldehydes such as formaldehyde, acetaldehyde and butylaldehyde, hydroxy-substituted acids such as salicylic acid, benzoic acid, 3,5-dihydroxybenzoic acid and 5,5-thiodisalicylic acid), silver salts or complexes of thioenes (for example, 3-(2-carboxyethyl)-4-hydroxymethyl-4-(thiazoline-2-thioene and 3-carboxymethyl-4-thiazoline-2-thioene), complexes of silver with nitrogen acid selected from imidazole, pyrazole, 1H-tetrazole, and 1,2,4-thiazole, urazole, 3-amino-5-benzylthio-1,2,4-triazole and benztoriazole or saccharin, of salts thereof; silver salts 5-chlorosalicylaldoxime and the like; and silver salts of mercaptides. Of these, the preferred silver salt is silver behenate. The content of the organic silver salt is 3  $g/m^2$  or less and, preferably,  $2 \text{ g/m}^2$  or less in terms of the amount

of silver.
[0072]

organic silver salts can be prepared by mixing a water-soluble silver compound with a compound which forms a complex with silver and, on this occasion, a normal precipitation, a reverse precipitation, a double-jet precipitation, a controlled double-jet precipitation as described in JP-A No. 9-127643 and the like are preferably used.

[0073]

A silver halide grain used in the present invention is such a silver halide grain as functions as an optical sensor. In order to suppress translucence after image formation and to obtain excellent image quality, an average grain size is preferably in a small-sized side. The average grain size is preferably 0.20 µm or less, more preferably from 0.03 to 0.15 µm and, particularly preferably, from 0.03 to 0.11 µm. The term "grain size" as used herein denotes a ridge line length of a silver halide grain when it is a so-called regular crystal which is either cubic or octahedral. When the grain is not a regular crystal, for example, when it is a spherical, cylindrical or tabular grain, the grain size is a diameter of a sphere equivalent having a same volume as each of those silver halide grains.

[0074]

There is no particular limitation on a silver halide grain

shape. However, a high ratio occupying a Miller index[100] plane is preferred. This ratio is preferably 50% or more, more preferably 70% or more and, particularly preferably, 80% or more. The ratio occupying the Miller index[100] plane can be obtained based on T. Tani, J. Imaging Sci., 29, 165 (1985) in which adsorption dependency of a[111] plane and a[100] plane is utilized.

[0075]

A composition of a halogen is not particularly limited and may be any one of silver chloride, silver chlorobromide, silver chloroiodobromide, silver bromide, silver iodobromide and silver iodide. A photographic emulsion employed in the present invention can be prepared employing any one of methods P. Glafkides, "Chimie et Physique as described in Photographique" (published by Paul Montel, 1967), G. F. Duffin, "Photographic Emulsion Chemistry" (published by The Focal Press, 1966), V. L. Zelikman et al., "Making and Coating Photographic Emulsion" (published by The Focal Press, 1964) and the like. Namely, any one of several acid emulsions, neutral emulsions, ammonia emulsions and the like may be employed. Furthermore, when grains are prepared by allowing soluble silver salts to react with soluble halide salts, a single-jet method, a double-jet method, or combinations thereof may be employed. The resultant silver halide may be incorporated into an image forming layer utilizing any practical method, and at such time,

Furthermore, the silver halide may be prepared by converting a part or all of the silver in an organic silver salt formed through the reaction of an organic silver salt with halogen ions into silver halide. The silver halide may be previously prepared and the resultant silver halide may be added to a solution to prepare the organic silver salt, or combinations thereof may be used; however, the latter is preferred. Ordinarily, the content of silver halide in organic silver salt is preferably from 0.75 to 30% by weight.

The silver halide employed in the present invention is preferably contains ions of metals belonging to Groups 6 to 11 of the Periodic Table. As for the above-mentioned metals, W, Fe, Co, Ni, Cu, Ru, Rh, Pd, Re, Os, Ir, Pt and Au are preferred. [0077]

Ions of these metals may each be introduced into the silver halide in the form of a metal complex or a metal complex ion.

As for such metal complexes and metal complex ions, six-coordinate metal complexes represented by the following general formula are preferred:

[0078]

General formula:  $(ML_6)^m$ ,

wherein M represents a transition metal selected from

elements in Groups 6 to 11 of the Periodic Table; L represents a ligand; and m represents 0, -, 2-, 3- or 4-. Specific examples of such ligands as represented by L include the ligands of halides (fluoride, chloride, bromide, and iodide), cyanide, cyanato, thiocyanato, selenocyanato, tellurocyanato, azido and aquo, nitrosyl and thionitrosyl. Among these ligands, aquo, nitrosyl and thionitrosyl are preferred. When the aquo ligand is present, one or two ligands are preferably coordinated. The ligands as represented by L may be same with or different from one another.

Particularly preferable examples of M include rhodium (Rh), ruthenium (Ru), rhenium (Re), iridium (Ir) and osmium (Os).

Specific examples of transition metal complex ions are described below; however, the present invention is not limited thereto.

[0081]

1:[RhCl<sub>6</sub>]<sup>3-</sup>

2: [RuCl<sub>6</sub>]<sup>3-</sup>

3:[ReCl<sub>6</sub>]<sup>3-</sup>

4: [RuBr<sub>6</sub>]<sup>3-</sup>

5: [OsCl<sub>6</sub>]<sup>3-</sup>

6:[IrCl<sub>6</sub>]<sup>4-</sup>

7:[CrCl<sub>6</sub>]<sup>4-</sup>

```
8: [Ru(NO)Cl<sub>5</sub>]<sup>2-</sup>
9:[RuBr<sub>4</sub>(H<sub>2</sub>O)]<sup>2-</sup>
 10: [Ru(NO)(H<sub>2</sub>O)Cl<sub>4</sub>]
 11:[RhCl<sub>5</sub>(H<sub>2</sub>O)]<sup>2-</sup>
 12:[Re(NO)Cl<sub>5</sub>]<sup>2-</sup>
 13: [Re(NO)(CN)_5]^{2-}
 14:[Re(NO)Cl(CN)4]2-
  15:[Rh(NO)2Cl4]
  16:[Rh(NO)(H<sub>2</sub>O)Cl<sub>4</sub>]
  17: [Ru(NO)(CN)5]<sup>2-</sup>
   18:[Fe(CN)<sub>6</sub>]<sup>3-</sup>
   19:[Rh(NS)Cl<sub>5</sub>]<sup>2-</sup>
   20:[Os(NO)Cl<sub>5</sub>]<sup>2-</sup>
   21:[Cr(NO)Cl<sub>5</sub>]<sup>2-</sup>
   22:[Re(NO)Cl<sub>5</sub>]
    23: [Os(NS)Cl4(TeCN)]2-
    24: [Ru(NS)Cl<sub>5</sub>]<sup>2-</sup>
    25:[Re(NS)Cl4(SeCN)]<sup>2-</sup>
    26: [Os(NS)Cl(SCN)4]2-
     27:[Ir(NO)Cl<sub>5</sub>]<sup>2-</sup>
     28:[Ir(NS)Cl<sub>5</sub>]<sup>2-</sup>
```

One type of these metal ions, metal complexes or metal complex ions may be employed and the same type of metals or the different type of metals may be employed in combinations of two or more types. Ordinarily, the content of these metal

ions, metal complexes or metal complex ions is suitably from  $1 \times 10^{-9}$  to  $1 \times 10^{-2}$  mole and, preferably, from  $1 \times 10^{-8}$  to  $1 \times 10^{-4}$  mole, per mole of silver halide.

[0082]

Compounds, which provide these metals, are preferably incorporated into the silver halide grains through addition during silver halide grain formation. These metals may be added during any preparation stage of the silver halide grains, that is, before or after nuclei formation, growth, physical ripening, and chemical ripening. However, these metals are preferably added at the stage of nuclei formation, growth, and physical ripening, more preferably added at the stage of nuclei formation and growth and, most preferably, added at the stage of nuclei formation.

[0083]

These compounds may be added several times by dividing the added amount. Uniform content in the interior of a silver halide grain can be carried out. As disclosed in JP-A Nos. 63-29603, 2-306236, 3-167545, 4-76534, 6-110146, 5-273683, the metals can also be contained in the interior of the grain with a given distribution. Preferably, the metals can be contained in the interior of the grain with the distribution.

These metal compounds can be dissolved in water or suitable organic solvents (for example, alcohols, ethers, glycols,

ketones, esters or amides) and, then, added. On this occasion, there are, for example, a method in which an aqueous metal compound powder solution or an aqueous solution in which a metal compound is dissolved along with NaCl and KCl is added to a water-soluble silver salt solution during grain formation or to a water-soluble halide solution; another method in which, when a silver salt solution and a halide solution are simultaneously added, a metal compound is added as a third solution to form silver halide grains, while simultaneously mixing three solutions, another method in which, during grain formation, an aqueous solution comprising a necessary amount of a metal compound is loaded in a reaction vessel and another method in which, during silver halide preparation, dissolution is carried out by the addition of other silver halide grains previously doped with metal ions or complex ions. Particularly, the preferred method is one in which an aqueous metal compound powder solution or an aqueous solution in which a metal compound is dissolved along with NaCl and KCl is added to a water -soluble halide solution.

[0085]

When the addition is carried out onto grain surfaces, an aqueous solution comprising the necessary amount of the metal compound can be loaded in the reaction vessel immediately after the grain formation, during the physical ripening, at the completion thereof or during the chemical ripening.

[0086]

[0087]

A reducing agent is preferably incorporated into the photothermographic material according to the present invention. Examples of suitable reducing agents are described in U.S. Pat. Nos. 3,770,448, 3,773,512, and 3,593,863, and Research Disclosure Items 17029 and 29963, and include such compounds as described below.

Aminohydroxycycloalkenone compounds (for amino 2-hydroxypiperidino-2-cyclohexenone); esters reductones as precursors of reducing agents (for example, N-hydroxyurea monoacetate); reducton piperidinohexose derivatives (for example, N-p-methylphenyl-N-hydroxyurea); hydrazones of aldehydes or ketones (for example, anthracene hydrazone); phosphamidophenols; phenyl aldehyde · phosphamidoanilines; polyhydroxybenzenes (for example, hydroquinone, t-butylhydroquinone, isopropylhydroquinone, (2,5-dihydroxy-phenyl)methylsulfone); sulfhydroxamic example, benzenesulfhydroxamic acids (for 4-(N-methane example, sulfonamidoanilines (for sulfonamide)aniline); 2-tetrazolylthiohydroquinones (for example, 2-methyl-5-(1-phenyl-5-tetrazolylthio)hydroquinone);

tetrahydroquionoxalines (for example, 1,2,3,4-tetrahydroquinoxaline); amidoxines; azines (for

example, combinations of aliphatic carboxylic acid acid); combinations ascorbic and. arylhydrazides polyhydroxybenzenes and hydroxylamines, reductones and/or hydrazine; hydroxamic acids; combinations of azines and sulfonamidophenols;  $\alpha$ -cyanophenylacetic acid derivatives; combinations of bis- $\beta$ -naphthol and 1,3-dihydroxybenzene 5-pyrazolones; sulfonamidophenol reducing derivatives; agents; 2-phenylindane-1,3-dione and the like; chroman; example, (for 1,4-dihydropyridines 2,6-dimethoxy-3,5-dicarboethoxy-1,4-dihydropyridine); bisphenols (for example, bis(2-hydroxy-3-t-butyl-5-methyl bis(6-hydroxy-m-tri)mesitol, phenyl)methane, phenyl)propane, 2,2-bis(4-hydroxy-3-methyl 4,5-ethylidene-bis(2-t-butyl-6-methyl)phenol, UV-sensitive ascorbic acid derivatives and 3-pyrazolidones. Of these reducing agents, particularly preferable reducing agents are hindered phenols.

Examples of the hindered phenols include compounds as represented by the general formula (A) as described below.
[0088]

[Chemical 20]

general formula (A):

[0089]

In the formula, R represents a hydrogen atom or an alkyl group having from 1 to 10 carbon atoms (for example, butyl or 2,4,4-trimethylpentyl); and R' and R" each represent an alkyl group having from 1 to 5 carbon atoms (for example, methyl, ethyl or t-butyl).

[0090]

Specific examples of the compounds as represented by the general formula (A) are described below; however, the present invention is not limited thereto.
[0091]

[Chemical 21]:

[0092]

[Chemical 22]

A-5 
$$C_4H_9$$
  $C_4H_9(t)$   $C_4H_9(t)$ 

A-7 OH 
$$C_4H_9(1)$$
 $C_2H_5$   $C_2H_5$ 

[0093]

An amount of reducing agents, inclusive of the compounds as represented by the above-mentioned general formula (A) to be used is preferably from  $1\times10^{-2}$  to 10 moles and, particularly preferably, from  $1\times10^{-2}$  to 1.5 mole, per mole of silver. [0094]

Binders suitable for the photothermographic material according to the present invention may either be transparent or translucent and is ordinarily colorless. Examples of the

binders include natural polymers, synthetic resins, polymers and copolymers and, further, film forming media; for example, gelatin, gum arabic, polyvinyl alcohol, hydroxyethyl cellulose, cellulose acetate, cellulose acetate butylate, polyvinyl pyrrolidone, casein, starch, polyacrylic acid, polymethyl methacrylate, polyvinyl chloride, polymethacrylic acid, a styrene-maleic anhydride copolymer, a styrene-acrylonitrile copolymer, a styrene-butadiene copolymer, polyvinyl acetals (for example, polyvinyl formal and polyvinyl butyral), polyesters, polyurethanes, phenoxy resins, polyvinylidene chloride, polyepoxides, polycarbonates, polyvinyl acetates, cellulose esters, polyamides. These binders may either be hydrophilic or hydrophobic.

According to the present invention, an amount of the binder in the photosensitive layer is preferably from 1.5 to 6.0 g/m<sup>2</sup> and, more preferably, from 1.7 to 5.0 g/m<sup>2</sup>. When the amount thereof is less than  $1.5 \text{ g/m}^2$ , a density of an unexposed portion is increased to a great extent and, then, the photothermographic material according to the invention may sometimes become unusable.

[0096]

According to the present invention, a matting agent is preferably incorporated into a photosensitive layer side. In order to enhance a repeating accuracy of a size according to

the present invention, a polymer matting agent or an inorganic matting agent is preferably incorporated in an amount, based on the weight of the entire binder, of from 0.5 to 10% by weight in the emulsion layer side.

[0097]

A material of the matting agent employed in the present invention may either be an organic substance or an inorganic substance. Examples of such inorganic substances capable of being employed as matting agents include silica as described in Swiss Patent No. 330,158 and the like; glass powder as described in French Patent No. 1,296,995 and the like; and carbonates of alkali earth metals, cadmium, zinc and the like as described in U.K. Patent No. 1.173,181 and the like. Regarding organic substances, starch as described in U.S. Pat. No. 2,322,037; starch derivatives as described in Belgian Patent No. 625,451, U.K. Patent No. 981,198 and the like; polyvinyl alcohols as described in JP-B No. 44-3643; polystyrenes or polymethacrylates as described in Swiss Patent No. 330,158; polyacrylonitriles as described in U.S. Pat. No. 3,079,257; and polycarbonates as described in U.S. Pat. No. 3,022,169 can be used as matting agents.

[8000]

A shape of the matting agent may be crystalline or amorphous; however, a crystalline in a spherical shape is preferably employed. A size of the matting agent is expressed

in terms of a diameter of a sphere equivalent which has a same volume as the matting agent. According to the present invention, a grain diameter of the matting agent denotes a diameter of the sphere equivalent.

[0099]

The matting agent employed in the present invention has an average particle diameter of preferably from 0.5 to 10  $\mu m$ , and, more preferably, from 1.0 to 8.0  $\mu m$ . A variation coefficient of grain size distribution is preferably 50% or less, more preferably 40% or less and, particularly preferably, 30% or less.

[0100]

The term "variation coefficient of grain size distribution" as used herein denotes a value as represented by the formula described below.

[0101]

(Standard deviation of grain diameter)/(average grain diameter)  $\times$  100

The matting agent according to the present invention can be incorporated into arbitrary constitution layers. In order to accomplish the object of the present invention, the matting agent is preferably incorporated into constitution layers other than the photosensitive layer and, more preferably, incorporated into a farthermost layer from the support.

As for an addition method of the matting agent according to the present invention, a method in which the matting agent is previously dispersed in a coating composition and, then, the resultant mixture is applied may be used, or a method in which, prior to completion of drying, the matting agent is sprayed may be used. When plural types of matting agents are added, both of the above-described methods may simultaneously be employed.

[0103]

When the photothermographic material according to the present invention is used for an output of an image setter for printing, a hydrazine compound is preferably incorporated in the photosensitive material.

Preferable hydrazine compounds to be used in the present invention are described in Research Disclosure, Item 23516 (November 1983 Issue, page 346) and publications cited therein. Examples of such hydrazine compounds as described in the above-mentioned publications include those as described in U.S. Pat. Nos. 4,080,207, 4,269,929, 4,276,364, 4,278,748, 4,385,108, 4,459,347, 4,478,928, 4,560,638, 4,686,167, 4,912,016, 4,988,604, 4,994,365,5,041,355, and 5,104,769; U.K. Patent No. 2,011,391B; European Patent Nos. 217,310, 301,799, and 356,898; and JP-A Nos. 60-179734, 61-170733, 61-270744, 62-178246,62-270948,63-29751,63-32538,63-104047,63-121838,

63-129337, 63-223744, 63-234244, 63-234245, 63-234246, 63-294552, 63-306438, 64-10233, 1-90439, 1-100530, 1-105941, 1-105943, 1-276128, 1-280747, 1-283548, 1-283549, 1-285940, 2-2541, 2-77057, 2-139538, 2-196234, 2-196235, 2-198440, 2-198441, 2-198442, 2-220042, 2-221953, 2-221954, 2-285342, 2-285343, 2-289843, 2-302750, 2-304550, 3-37642, 3-54549, 3-125134, 3-184039, 3-240036, 3-240037, 3-259240, 3-280038, 3-282536, 4-51143, 4-56842, 4-84134, 2-230233, 4-96053, 4-216544, 5-45761, 5-45762, 5-45763, 5-45764, 5-45765, 6-289524 and 9-160164.

[0105]

Other than these compounds, compounds as described in (Chemical 1) of Japanese Patent Publication (hereinafter, referred to also as JP-B) No. 6-77138, specifically, compounds as described on pages 3 and 4 of the Publication; compounds as represented by the general formula (I) as described in JP-B No. 6-93082, specifically, compounds 1 through 38 as described on pages 8 to 18 of the Publication; compounds as represented by the general formula (4), general formula (5) and the general formula (6) as described in JP-A No. 6-230497, specifically, compounds 4-1 through 4-10 as described on pages 25 and 26, compounds 5-1 through 5-42 as described on pages 28 to 36, and compounds 6-1 through 6-7 as described on pages 39 and 40 of the Publication; compounds as represented by the general formula (1) and the general formula (2) as described in JP-A No. 6-289520,

specifically, compounds 1-1) through 1-17) and 2-1) as described on pages 5 to 7 of the Publication; compounds as described in (Chemical 2) and (Chemical 3) of JP-ANo. 6-313936, specifically, compounds as described on pages 6 to 19 of the Publication; compounds as described in (Chemical 1) of JP-A No. 6-313951, specifically, compounds as described on pages 3 to 5 of the Publication; compounds as represented by the general formula (I) as described in JP-A No. 7-5610, specifically, compounds I-1 through I-38 as described on pages 5 to 10 of the Publication; compounds as represented by the general formula (II) as described in JP-A No. 7-77783, specifically, compounds II-1 through II-102 as described on pages 10 to 27 of the Publication; and compounds as represented by the general formula (H) and the general formula (Ha) as described in JP-A No. 7-104426, specifically, compounds H-1 through H-44 as described on pages 8 to 15 of the Publication.

An amount of the hydrazine compound according to the present invention to be added is in the range of preferably  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  mole and, particularly preferably,  $1 \times 10^{-5}$  to  $5 \times 10^{-2}$  mole, per mole of silver.

The hydrazine compound according to the present invention may be dissolved in a suitable organic solvent such as, for example, alcohols (methanol, ethanol, propanol, and fluorinated alcohol), ketones (acetone, methyl ethyl ketone),

dimethyl formamide, dimethyl sulfoxide, methyl cellosolve and, then, used. Further, by a well known emulsion dispersion method, the hydrazine compound is dissolved in an oil such as dibutyl phthalate, tricresyl phthalate, glyceryl triacetate or diethyl phthalate with an aid of an auxiliary solvent such as ethyl acetate or cyclohexane and, then, the resultant mixture is mechanically dispersed to prepare an emulsified dispersion which can, subsequently, be employed for practical use. the method mentioned above, by a known method as a solid dispersion method, powder of the hydrazine compound is dispersed in water by means of a ball mill, a colloid mill or an ultrasonic homogenizer to prepare a solid dispersion which can, subsequently, be employed for practical use. According to the present invention, indazoles (for example, nitroindazole) are preferably used as antifoggants in combination with the hydrazine compound.

[0108]

In the photothermographic material according to the present invention, a neucleation accelerating agent such as an amine derivative, an onium salt compound, a disulfide derivative or a hydroxylamine derivative can be used in combination with the hydrazine compound.

[0109]

The photothermographic material according to the present invention is stable at normal temperatures and is developed,

after exposure, when heated up to high temperatures (for example, from 80°C to 140°C). Upon heating, silver is formed through an oxidation-reduction reaction between the organic silver salt (functioning as an oxidizing agent) and the reducing agent. This oxidation-reduction reaction is accelerated by the catalytic action of a latent image formed in the silver halide through exposure. Silver formed by the reaction with the organic silver salt in an exposed area yields a black image, which contrasts with an unexposed area, to thereby form an image. This reaction process proceeds without the further supply of a processing solution such as water from outside.

The photothermographic material according to the present invention comprises a support having thereon at least one photosensitive layer, and the photosensitive layer may only be formed on the support; however, it is preferable that at least one non-photosensitive layer is formed on the photosensitive layer. The photosensitive layer may be constituted by a plurality of layers. Further, for gradation adjustment, in terms of sensitivity, layers may be constituted in such a manner as a fast layer/slow layer or a slow layer/fast layer. Various types of additives may be incorporated into any one of a photosensitive layer, a nonphotosensitive layer and other formed layers.

[0111]

[.0110]

A surface active agent, an antioxidant, a stabilizer, a plasticizer, a UV ray absorber, a covering aid or the like may be employed in the photothermographic material according to the present invention.

[0112]

It is preferable that a color control agent is incorporated into the photothermographic material according to the present invention. Examples of suitable color control agents, while being disclosed in Research Disclosure Item 17029, include the following articles:

[0113]

imides (for example, phthalimide); cyclic imides, pyrazoline-5-one, and quinazolinone (for example, succinimide, 3-phenyl-2-pyrazoline-5-one, 1-phenylurazole, quinazoline 2,4-thiazolidione); naphthalimides (for example, N-hydroxy-1,8-naphthalimide); cobalt complexes (for example, cobalt hexaminetrifluoroacetate), mercaptans (for example, N-(aminomethyl)aryl 3-mercapto-1,2,4-triazole); N-(dimethyl (for example, dicarboxyimides aminomethyl)phthalimide); blocked pyrazoles, combinations of isothiuronium derivatives and certain types of light -bleaching combination example, (for agents N, N'-hexamethylene(1-carbamoyl-3,5-dimethyl pyrazole), 1,8-(3,6-dioxaoctane)-bis-(isothiuroniumtrifluoroacetate), and 2-(tribromomethyl sulfonyl)benzothiazole; merocyanine

3-ethyl-5-((3-etyl-2-benzothiazolinylidene-(benzothiazolin ylidene))-1-methylethylidene-2-thio-2,4-oxazolidinedione); phthalazinone, phthalazinone derivatives or metal salts 4-(1-naphthyl)phthalazinone, example, (for thereof phthalazinone and 5,7-dimethyl 6-chlorophthalazinone, combinations 2,3-dihydro-1,4-phthalazinedione); phthalazinone and sulfinic acid derivatives (for example, benzenesulfinate sodium 6-chlorophthalazinone plus p-trisulfonate); sodium 8-methylphthalazinone plus combinations of phthalazine and phthalic acid; combinations of phthalazine (including phthalazine addition products) and at least one compound selected from among maleic anhydride and phthalic acid, 2,3-naphthalene dicarboxylic acid, o-phenylenic acid derivatives and anhydrides thereof (for example, phthalic acid, 4-methyl phthalic acid, 4-nitrophthalic acid, and quinazolinediones, anhydride); tetrachlorophthalic derivatives, naphthoxazine benzoxazine, example, (for benzoxazine-2,4-diones pyrimidines 1,3-benzoxazine-2,4-dione); asymmetry-triazines (for example, 2,4-dihydroxypyrimidine) example, derivatives tetraazapentalene and 3,6-dimercapto-1,4-diphenyl-1H,4H-2,3a,5,6a-tatraazapental As for preferable color control agents, phthalazone or phthalazine is mentioned.

[0114]

In the photothermographic material according to the present invention, sensitizing dyes as described in JP-A Nos. 63-159841, 60-140335, 63-231437, 63-259651, 63-304242 and 63-15245; U.S. Pat. Nos. 4,639,414, 4,740,455, 4,741,966, 4,751,175 and 4,835,096 can be used. Sensitizing dyes usable in the present invention are described in Research Disclosure Item 17643, Sect. IV-A (December, 1978 page 23), ibid, Item 1831 Sect. X (August, 1978, page 437) or literatures cited therein.

[.0115]

Sensitizing dyes having spectral sensitivity suited for spectral characteristics of various scanner light sources can advantageously be selected. Examples thereof include A) for an argon laser light source, simple merocyanines as described in JP-A Nos. 60-162247 and 2-48653; U.S. Pat. No. 2,161,331; West German Patent 936,071; and Japanese Patent Application No. 3-189532; B) for a helium-neon laser light source, three-nuclei cyanine dyes as described in JP-A Nos. 50-62425, 54-18726 and 59-102229, and merocyanines as described in Japanese Patent Application No. 6-103272; C) for an LED light source and an infrared semiconductor laser light source, thiacarbocyanine dyes as described in JP-B Nos. 48-42172, 51-9609 and 55-39818, and JP-A No. 62-284343 and 2-105135; D) for an infrared semiconductor laser light source,

tricarbocyanines as described in JP-A Nos. 59-191032 and 60-80841, and dicarbocyanines containing 4-quinoline nucleus as described in JP-A Nos. 59-192242 and in the general formulas (IIIa) and (IIIb) of JP-A No. 3-67242.

When a wavelength of the infrared laser light source is 750 nm or more and, preferably, 800 nm or more, in order to meet such wavelength range as described above, sensitizing dyes as described in JP-A Nos. 4-182639 and 5-341432; JP-B Nos. 6-52387 and 3-10931; U.S. Pat. No. 5,441,866; and JP-A No. 7-13295 can favorably be used. These sensitizing dyes may be used either alone or in combinations thereof. These combinations are frequently used particularly for the purpose of supersensitization. A dye itself exhibiting no spectral sensitization action or a substance exhibiting no substantial absorption of the visible light, while both exhibiting supersensitization together with a sensitizing dye, may be incorporated in the emulsion.

[0117]

Infrared semiconductor lasers (780 nm, 810 nm, 830 nm) are preferably employed for exposure of photothermographic materials according to the present invention.

[0118]

[Embodiments]

Hereinafter, the present invention will be explained with

reference to embodiments; however, the present invention is not limited thereto.

[0119]

## Example 1

<<Synthesis of Exemplified Compound According to the Present Invention>>

Synthesis Path of Exemplified Compounds 4-2 and 1-2

[0120]

[Chemical 23]

Exemplified compound 4-2 Exemplified compound 1-2

[0121]

(Synthesis of Exemplified Compound 4-2)

described in Heterocycles, 26 (4), 1029 to 1036 (1987) and 20 ml of ethyl alcohol were added with 8.1 g of 5-undecane and refluxed for 9 hours and, then, further added with 15 g of 5-undecane and refluxed for 3 hours. The resultant reaction product was concentrated and purified by using a column chromatography, to thereby obtain 2.0 g of the exemplified compound 4-2 as a brown solid. The exemplified compound 4-2 was identified by using an NMR spectrum and a Mass spectrum.

[0122]

(Synthesis of Exemplified Compound 1-2)

2.0 gofthe thus-obtained exemplified compound 4-2 (being used as an intermediate), 0.4 g of 3,4-dihydroxy-3-cyclobutene-1,2-dione, 30 ml of n-butanol and 30 ml of toluene were allowed to react thereamong for 3 hours while purging water to be generated at an outside temperature of 140°C. The resultant reaction product was concentrated and purified by using a column chromatography, to thereby obtain 0.4 gofthe exemplified compound 1-2. The exemplified compound 1-2 was identified by using an NMR spectrum and a Mass spectrum. [0123]

Other compounds than these two exemplified compounds can similarly be synthesized.

[0124]

Example 2

<<pre><<Pre><<Pre>reparation and Evaluation of Photothermographic Material>>
(Preparation of Silver Halide Grain A)

7.5 g of gelatin and 10 mg of potassium bromide were dissolved in 900 ml of purified water and, then, a temperature and a pH value of the resultant solution were adjusted to be 35°C and 3.0, respectively and, thereafter, the thus -adjusted solution was added with 370 ml of an aqueous solution containing 74 g of silver nitrate and an aqueous solution containing potassium bromide and potassium iodide at a molar ratio of 96/4

consuming 10 minutes by using a controlled double -jet method, while keeping the pAg value to be 7.7. Subsequently, the added mixture resultant 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene and, then, the pH value of the resultant mixture was adjusted to 5 by using NaOH, to thereby obtain cubic silver iodobromide grains having an average grain size of 0.06  $\mu m$ , a variation coefficient of 8% of a projection diameter area and a[100] plane ratio of 86%. subjected to . was emulsion resultant The coagulate-precipitation by using a gelatin coagulant and, then, subjected to a desalting treatment and, thereafter, add with 0.1 g of phenoxyethanol and, subsequently, the pH value and the pAg value of the resultant mixture were adjusted to 5.9 and 7.5, respectively. Then, the resultant mixture was added with a sensitizing dye-1 and a sensitizing dye-2 each by  $5 \times 10^{-5}$ mole per mole of silver halide and, after the temperature thereof being raised to 60°C, added with 2 mg of sodium thiosulfate, left to stand for 100 minutes for ripening and, then, cooled down to 38°C to terminate a chemical sensitization and, as a result, the silver halide grain A was obtained.

[0125]

[Chemical 24]

Sensitizing dye-1

Sensitizing dye-2

[0126]

(Preparation of Organic Fatty Acid Silver Emulsion A)

dissolved by being heated at 90 °C, stirred thoroughly and, then, the resultant solution was added with 31.1 ml of 1N-NaOH and left to stand for one hour as it is. Thereafter, the resultant solution was cooled down to 30 °C, added with 7.0 ml of 1N-phosphoric acid, stirred thoroughly and, then, added with 0.01 g of N-bromosuccinimide. Subsequently, the resultant mixture was added with the previously prepared silver halide grain A such that an amount of silver becomes 10% by mole relative to benenic acid in a state in which the mixture was heated at 40°C while stirring. Further, the resultant mixture was continuously added with 25 ml of an aqueous 1N-silver nitrate solution consuming two minutes and left to stand as it is for one hour while being kept stirring.

[0127]

The resultant emulsion was added with polyvinyl butyral dissolved in ethyl acetate and, after being thoroughly stirred, left to stand and allowed to be separated to an ethyl acetate phase containing silver behenate grains and silver halide grains, and a water phase. After removing the water phase, the silver behenate grains and silver halide grains were recovered by centrifugation. Thereafter, those grains were added with 20 g of synthetic zeolite A-3 (spherical) manufactured by Tosoh Corporation and 22 cc of isopropyl alcohol, left to stand for one hour and, then, subjected to filtration and, further, added with 3.4 g of polyvinyl butyral and 23 cc of isopropyl alcohol, thoroughly stirred at a high speed at 35 °C, allowed to be dispersed and, then, preparation of the organic fatty acid silver emulsion A was terminated.

[0128]

(Photosensitive layer composition)

Organic fatty acid silver emulsion	A $1.75 \text{ g/m}^2$		
(in t	n terms of silver)		
Pyridinium hydrobromidoperbromide	$1.5 \times 10^{-4} \text{ mol/m}^2$		
Calcium bromide	$1.8 \times 10^{-4} \text{ mol/m}^2$		
2,4-dichlorobenzoic acid	$1.5 \times 10^{-3} \text{ mol/m}^2$		
Sensitizing dye-1	$2.1 \times 10^{-6} \text{ mol/m}^2$		
Sensitizing dye-2	$2.1 \times 10^{-6} \text{ mol/m}^2$		
·	$3.2 \times 10^{-3} \text{ mol/m}^2$		

2-tribromomethyl sulfonyl pyridine  $6.0 \times 10^{-4} \text{ mol/m}^2$ Dye of present invention, dye-1 for comparison (shown in Table 1)  $5.0 \times 10^{-5} \text{ mol/m}^2$ 

As for solvents, methyl ethyl ketone, acetone and methanol are appropriately used.

[0129]

(Surface protective layer composition)

A surface protective layer coating solution was prepared as follows:

[0130]

Cellulose acetate

 $4 \text{ g/m}^2$ 

1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethy

lhexane

 $4.8 \times 10^{-3} \text{ mol/m}^2$ 

Phthalazine

 $3.2 \times 10^{-3} \text{ mol/m}^2$ 

4-methyl phthalic acid

 $1.6 \times 10^{-3} \text{ mol/m}^2$ 

Tetrachlorophthalic acid

 $7.9 \times 10^{-4} \text{ mol/m}^2$ 

Tetrachlorophthalic anhydride

 $9.1 \times 10^{-4} \text{ mol/m}^2$ 

Silicon dioxide (grain diameter: 2  $\mu$ m) 0.22g/m<sup>2</sup>

As for solvents, methyl ethyl ketone, acetone and methanol

are appropriately used.

[0131]

(Backing layer composition)

A backing layer coating solution was prepared as follows: [0132]

 $4 \text{ g/m}^2$ 

Cellulose acetate

Dye of present invention, dye-1 for comparison (shown in Table 1)

 $5.0 \times 10^{-5} \text{ mol/m}^2$ 

Polymethyl methacrylate (grain diameter: 10  $\mu m$ ) 0.02 g/m<sup>2</sup>

The above-described composition was applied on a biaxially- stretched polyethylene terephthalate film having a thickness of 175  $\mu m$  and, then, dried, to thereby prepare a coated sample.

[0133]

Such photothermographic material as prepared in the above step was cut to a size according to the 135-standard, exposed to a beam of a laser diode of 810 nm which was inclined at 13° from a vertical face and, then, thermally developed under conditions of 120°Cx15 seconds by using a heat drum.

<<Evaluation method>>

[Evaluation of Sharpness]

An MTF value of each developed sample at 10 lines/mm was measured and shown in Table 1 as a relative value to that of sample No. 101 which is defined as 100.

[0135]

[Visual Evaluation of Color Turbidity]

Subjective evaluations were conducted by ten monitors.

Points, based on the following criteria, of all monitors were added up for evaluation:

3: Level of no practical problem;

1: Allowable minimum level; and

0: Level entirely unacceptable for practical use.

[0136]

## [Table 1]

Sample No.	Dye	Sharpness	Color turbidity	Remark
101	Dye 1 for	100	8	Comparison
102	comparison 1-2	120	30	Present invention
103	1-16	120	28	Present invention
104	1-25	118	29	Present invention

[0137]

[Chemical 25]

Dye 1 for comparison

Compound as described in JP-A No. 2-216140

[.0138]

From Table 1, it is found that the samples according to the present invention have excellent sharpness and less color

turbidity.

[0139]

Example 3

<<Pre><<Pre>c<Pre>caration and Evaluation of Photothermographic Material>>
[Preparation of Subbed Photographic Support]
<Pre>paration of PET-Subbed Photographic Support>

Acorona discharge was performed at 8w/m² min on both faces of a commercially-available biaxially-stretched thermally-fixed PET film having a thickness of 100 µm and, then, on one face thereof, a subbing coating solution a-1 as descried below was applied such that it gave a dried film thickness of 0.8 µm and, then, dried, to thereby obtain a subbing layer A-1. On the other surface on the reverse side, a subbing coating solution b-1 as described below was applied such that it gave a dried film thickness of 0.8 µm and, then, dried, to thereby obtain a subbed layer B-1.

[0140]

<< Subbing Coating Solution a-1>>

A copolymer latex solution (solid content: 30%) of
Butyl acrylate (30 wt%),
t-butyl acrylate (20 wt%),
Styrene (25 wt%) and
2-hydroxyethyl acrylate (25 wt%)
(C-1)
Hexamethylene-1,6-bis(ethyleneurea)
0.8 g

Water to make the total volume up to 1 liter <<Subbing Coating Solution b-1>>

A copolymer latex solution (solid content: 30%) of Butyl acrylate (40 wt%), Styrene (20 wt%) and Glycidyl acrylate (40 wt%)

270 g

(C-1) 0.6 g

Hexamethylene-1,6-bis(ethyleneurea) 0.8 g

Water to make the total volume up to 1 liter

Subsequently, a corona discharge was performed at  $8w/m^2$  min on respective upper surfaces of the subbed layer A-1 and the subbed layer B-1 and, then, on the subbed layer A-1, a subbing upper layer coating solution a-2 as descried below was applied such that it gave a dried film thickness of 0.1  $\mu$ m, to thereby obtain a subbed layer A-2. On the subbed layer B-1, a subbing upper layer coating solution b-2 as described below was applied such that it gave a dried film thickness of 0.8  $\mu$ m, to thereby obtain a subbed upper layer B-2 having an antistatic function.

[0141]

<< Subbing Upper Layer Coating Solution a-2>>

| Gelatin   |     |     |     | Weight to make |       |  |
|-----------|-----|-----|-----|----------------|-------|--|
| (C-1)     |     | · . | 100 |                | 0.2 g |  |
| (C-2)     | ; . |     |     |                | 0.2 g |  |
| <br>(C-3) |     | •   |     |                | 0.1 g |  |

Silica grains (average grain diameter: 3  $\mu$ m) 0.1 g

Water to make the total volume up to 1 liter <<Subbing Upper Layer Coating Solution b-2>> 60 g (C-4)A latex solution (solid content: 20%) comprising (C-5) 80 g as a component 0.5 g Ammonium sulfate 12 g (C-6) Polyethylene glycol (a weight average molecular weight: 600) Water to make the total volume up to 1 liter [0142] [Chemical 26]

$$(C-1) \qquad C_{9}H_{19} \qquad O(CH_{2}CH_{2}O)_{12}SO_{3}Na$$

$$(C-2) \qquad C_{9}H_{19} \qquad O(CH_{2}CH_{2}O)_{9}SO_{3}Na$$

$$(C-3) \qquad CH_{2}=CHCO-N \qquad N-COCH=CH_{2}$$

$$COCH=CH_{2}$$

$$(C-4) \qquad -(CH_{2}-CH_{2})_{X} \qquad -(CH_{2}-CH_{2})_{Y} \qquad COOH \qquad M_{n}=5000$$

$$(M_{n}: number average molecular weight.)$$

$$X:y=75:25 \text{ (weight ratio)}$$

$$(C-5) \qquad -(CH_{2}-CH_{2})_{P} \qquad -(CH_{2}-CH_{2})_{Q} \qquad -(CH_{2}-CH_{2})_{T} \qquad COOC_{4}H_{9}$$

p:q:r:s:t= 40:5:10:5:40 (weight ratio)

[0143]

[Chemical 27]

(C-6)

Mixture of 3 types of:

[0144]

(Preparation of Silver Halide Emulsion B)

were dissolved in 900 ml of purified water and, then, a temperature and a pH value of the resultant solution were adjusted to be 35°C and 3.0, respectively and, thereafter, the thus-adjusted solution was added with 370 ml of an aqueous solution containing 74 g of silver nitrate and an aqueous solution containing potassium bromide and potassium iodide at a molar ratio of 98/2 and rhodium chloride in a amount of 1x10<sup>-4</sup> mol per one mol of silver consuming 10 minutes by using a controlled double-jet method, while keeping the pAg value to be 7.7. Subsequently, the resultant mixture was added with 0.3gof4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene and, then, the pH value of the resultant mixture was adjusted to 5 by using NaOH, to thereby obtain cubic silver iodobromide grains having an average grain size of 0.06 μm, a variation coefficient of

The resultant emulsion was subjected to a coagulate-precipitation by using a gelatin coagulant and, then, subjected to a desalting treatment and, thereafter, add with 0.1 g of phenoxyethanol and, subsequently, the pH value and the pAg value of the resultant mixture were adjusted to 5.9 and 7.5, respectively, to thereby obtain a silver halide emulsion B.

[0145]

Silver behenate was prepared by using a method as described below in accordance with a same method as in Example 1 according to JP-A No. 9-127643.

[0146]

(Preparation of Sodium Behenate Solution B)

34 g of behenic acid was dissolved in 340 ml of isopropanol at 65°C and, then, added, while stirring, a 0.25N aqueous solution of sodium hydroxide such that a pH value of the resultant solution came to be 8.7. On this occasion, about 400 ml of the aqueous sodium hydroxide solution was required. Next, the resultant aqueous sodium behenate solution was subjected to vacuum concentration, to thereby prepare a sodium behenate solution B in which a sodium behenate concentration was 8.9% by weight.

(Preparation of Silver Behenate Dispersion B)

A solution prepared by dissolving 30 g of ossein gelatin

in 750 ml distilled water was added with a 2.94M silver nitrate solution to have a silver electrical potential of 400 mV. The resultant solution was added with 374 ml of the above-mentioned sodium behenate solution B at 78°C employing a controlled double-jet method at a rate of 44.6 ml/min. and, at the same time, added with an aqueous 2.94M silver nitrate solution to have a silver electrical potential of 400 mV. During the addition, the added amounts of sodium behenate and silver nitrate were 0.092 mole and 0.101 mole, respectively. After the addition, stirring was continued further for 30 minutes and, then, water-soluble salts were removed by using ultrafiltration, to thereby obtain a silver behenate dispersion B.

[0148]

(Preparation of Photosensitive Emulsion B)

To the resultant silver behenate dispersion B, 0.01 mole of the above-mentioned silver halide emulsion B was added. With continuous stirring, dispersion flocks were formed by gradually adding 100 g of a n-butyl acetate solution containing polyvinyl acetate (1.2% by weight). Subsequently, water was removed and, further, water washing and water removal were carried out two more times. Then, with stirring, added was 60 g of a mixture consisting of butyl acetate containing 2.5% by weight of polyvinyl butyral (average molecular weight of 3,000) as a binder and isopropyl alcohol in a ratio of 1:2. Thereafter, the resultant gel-like mixture consisting of behenic acid and silver

halide was added with polyvinyl butyral (average molecular weight of 4,000) as a binder and isopropyl alcohol and was, then, dispersed, to obtain a photosensitive emulsion B. [0149]

Onto a support, each layer as described below was sequentially applied to prepare a sample of the photothermographic material. Further, the sample was dried at 75°C for 5 minutes.

Coating at Back Face Side:

A liquid having a composition as described below was applied such that it gave a wet thickness of 80  $\mu m_{\star}$  [0151]

Polyvinyl butyral (10% isopropanol solution)

150 ml

Dye of present invention, dye for comparison (shown in Table 2)

Coating at Photosensitive Layer Side:
Photosensitive Layer 1:

A liquid having a composition as described below was applied such that a coated silver amount was  $2.0\,\mathrm{g/m^2}$  and polyvinyl butyral as a binder was  $3.2\,\mathrm{g/m^2}$ . [0152]

Photosensitive Emulsion B Amount to make  $3 \text{ g/m}^2$  (in terms of silver)

Sensitizing dye-1 (0.1% DMF solution) 1 mg

Sensitizing dye-2 (0.1% DMF solution) 1 mg

Pyridinium bromidoperbromide (2% acetone solution)

0.3 ml:

2-tribromomethyl sulfonyl pyridine (2% acetone solution)

3 ml

Phthalazine (4.5% DMF solution)

8 ml

Developing agent-1 (Exemplified compound A-4 in general formula (A)); and (10% acetone solution) 13 ml

Hard gradation enhancing agent H (1% methanol/DMF=4:1 solution)

Dye of present invention, dye for comparison (Shown in Table 2); and (2% acetone solution) 0.1 ml

[Chemical 28]

... Hard gradation enhancing agent H

[0154]

Surface Protective Layer:

A liquid having a composition as described below was applied on each photosensitive layer so as to obtain a wet thickness of 100  $\mu m_{\bullet}$ 

[0155]

| Acetone                       | 175 ml |
|-------------------------------|--------|
| 2-propanol                    | 40 ml  |
| Methanol                      | 15 ml  |
| Cellulose acetate             | 8.0 g  |
| Phthalazine                   | 1.0 g  |
| 4-methyl phthalic acid        | 0.72 g |
| Tetrachlorophthalic acid      | 0.22 g |
| Tetrachlorophthalic anhydride | 0.5 g  |
|                               |        |

Monodispersed silica having an average grain diameter

of 4 μm

1% (w/W) relative to binder

<<Evaluation Method>>

[Evaluation of Sensitometry]

Such photothermographic material as prepared in the above step was cut to a size according to the 135-standard, exposed to a beam of a laser diode of 810 nm which was inclined at 13° from a vertical face and, then, thermally developed under conditions of 120°Cx15 seconds by using a heat drum.

[0156]

[Evaluation of Sharpness]

An MTF value of each developed sample at 10 lines /mm was measured and shown in Table 2 as a relative value to that of sample No. 201 which is defined as 100.

[0157]

[Visual Evaluation of Color Turbidity]

Subjective evaluations were conducted by ten monitors.

Points, based on the following criteria, of all monitors were added up for evaluation:

3: Level of no practical problem;

1: Allowable minimum level; and

0: Level entirely unacceptable for practical use.

#### [0158]

# [Table 2]

| Sample No. | Dye                  | Sharpness | Color<br>turbidity | Remark            |
|------------|----------------------|-----------|--------------------|-------------------|
| 201        | Dye 1 for comparison | 100       | 8                  | Comparison        |
| 202        | 1-2                  | 118       | 30                 | Present invention |
| 203        | 1-16                 | 116       | 28                 | Present invention |
| 204        | 1-25                 | 115       | 28                 | Present invention |

#### [0159]

From Table 2, it is found that the samples according to the present invention have excellent sharpness and less color turbidity.

#### [0160]

## Example 4

<<Pre><<Pre>reparation and Evaluation of Silver Halide Color
Photographic Photosensitive Material>>
(Preparation of Emulsion EM-P1)

While controlling an aqueous solution containing ossein gelatin at 40°C, an aqueous solution containing ammonia and

silver nitrate, and an aqueous solution containing potassium bromide and sodium chloride (KBr:NaCl=95:5 in molar ratio) were simultaneously added thereto by using a controlled double -jet method to obtain a cubic silver chlorobromide core emulsion having an average grain diameter of 0.30  $\mu$ m. On this occasion, a pH value and a pAg value were controlled such that a cubicle was obtained as a grain shape.

[0161]

Further, to the thus-obtained core emulsion, an aqueous solution containing ammonia and silver nitrate and an aqueous solution containing potassium bromide and sodium chloride (KBr:NaCl=40:60 in molar ratio) were simultaneously added by using a controlled double-jet method until obtaining a shell having an average grain diameter of 0.42  $\mu$ m. On this occasion, a pH value and a pAg value were controlled such that a cubicle was obtained as a grain shape.

[0162]

Then, after water-soluble salts were removed by water rinsing, gelatin was added, to thereby obtain an emulsion EM -P1. An expanse of distribution of the emulsion EM-P1 was 8%.
[0163]

(Preparation of Emulsion EM-P2)

While controlling an aqueous solution containing ossein gelatin at 40°C, an aqueous solution containing ammonia and silver nitrate, and an aqueous solution containing potassium

bromide and sodium chloride (KBr:NaCl=95:5 in molar ratio) were simultaneously added thereto by using a controlled double-jet method to obtain a cubic silver chlorobromide core emulsion having an average grain diameter of 0.18 µm. On this occasion, a pH value and a pAg value were controlled such that a cubicle was obtained as a grain shape.

Further to the thus-obtained core emulsion, an aqueous solution containing ammonia and silver nitrate and an aqueous solution containing potassium bromide and sodium chloride (KBr:NaCl=40:60 in molar ratio) were simultaneously added by using a controlled double-jet method until obtaining a shell having an average grain diameter of 0.25  $\mu m$ . On this occasion, a pH value and a pAg value were controlled such that a cubicle was obtained as a grain shape.

[0165]

[0164]

Then, after water-soluble salts were removed by water rinsing, gelatin was added, to thereby obtain an emulsion EM -P2. An expanse of distribution of the emulsion EM-P2 was 8%.
[0166]

(Preparation of Blue-Sensitive Silver Halide Emulsion)

After a sensitizing dye BS-1 was added to the above-described emulsion EM-Pl such that a color sensitization was allowed to be optimum, a stabilizer ST-1 was added to the resultant emulsion in an amount of 600 mg per mole of silver,

to thereby obtain a blue-sensitive emulsion Em-B1. [0167]

(Preparation of Green-Sensitive Silver Halide Emulsion)

A green-sensitive emulsion Em-G1 was prepared in a same manner as in the blue-sensitive emulsion Em-B1 except that a sensitizing dye GS-1 was added to the above-described emulsion EM-P2 such that color sensitization was allowed to be optimum. [0168]

(Preparation of Red-Sensitive Silver Halide Emulsion)

A red-sensitive emulsion Em-R1 was prepared in a same manner as in the blue-sensitive emulsion Em-B1 except that sensitizing dyes RS-1 and RS-2 were added to the above-described emulsion EM-P2 such that color sensitization was allowed to be optimum.

[0169]

ST-1: 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene

[Chemical 29]

GS-1

RS-1

RS-2

[0171]

(Preparation of Infrared-Sensitive Silver Halide Emulsion)

An infrared-sensitive emulsion Em-IR was prepared in a same manner as in the blue-sensitive emulsion Em-Bl except that a sensitizing dye IRS-1 was added to the emulsion EM-Pl such that color sensitization was allowed to be optimum.

[0172]

[Chemical 30]

IRS-1

[0173]

By using the thus-obtained Em-IR and each of the above-described Em-B1, Em-G1 and Em-R1 emulsions, each layer having a composition as described below was applied on a paper-pulp reflective support, having a thickness of 110 µm, laminated with high density polyethylene on a reverse face and fused polyethylene containing anatase-type titanium oxide in an amount of 15% by weight in a dispersed state on a surface, to thereby prepare a multi-color photosensitive material sample 301. Any one of H-1 and H-2 was added as a film-hardening agent; and any one of surface active agents SU-1, SU-2 and SU-3 was added as a coating auxiliary as well as an aid for dispersion.

12th layer (protective layer) Coating amount  $(g/m^2)$ 

|       | Gelatin                 |        | 1.60 |
|-------|-------------------------|--------|------|
| · · · | Silica matting agent    |        | 0.01 |
| 11th  | layer (UV-ray absorbing | layer) |      |
|       | Gelatin                 |        | 1.60 |
|       | my-ray absorbing agent  | (UV-1) | 0.35 |

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0.12
   UV-ray absorbing agent (UV-2)
    UV-ray absorbing agent (UV-3)
                                       0.60
10th layer (blue-photosensitive layer)
                                         1.10
     Gelatin
     Blue-photosensitive emulsion (Em-B1) 0.36
     Yellow coupler (Y-1)
      Anti-foggants (AF-2 and AF-3 in equivalent moles)
                                         0.0004
     Anti-staining agent (HQ-1)
      High boiling organic solvent (SO-1) 0.27
9th layer (intermediate layer)
      Gelatin ·
      Anti-staining agents (HQ-2 and HQ-3 in equivalent
                                          0.02
weights)
      High boiling organic solvent (SO-2) 0.05
     Anti-irradiation dye (AI-3)
 8th layer (yellow filter layer)
                                          0.45
       Gelatin
                                          .0.11
       Yellow colloidal silver
                                         0.03
       Anti-staining agent (HQ-1)
       High boiling organic solvent (SO-2) 0.008
                                          0.04
       Polyvinyl pyrrolidone
 7th layer (intermediate layer)
                                           0.45
      Gelatin
                                           0.014
       Anti-staining agent (HQ-2)
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Anti-staining agent (HQ-3)
     High boiling organic solvent (SO-2) 0.006
6th layer (green-photosensitive layer)
                                          1.25
      Gelatin
      Green-photosensitive emulsion (Em-G1) 0.32
                                          0.22
      Magenta coupler (M-1)
                                          0.05
      Yellow coupler (Y-2)
                                          0.035
      Anti-staining agent (HQ-1)
      Anti-foggants (AF-2 and AF-3 in equivalent moles)
                                          0.00036
      High boiling organic solvent (SO-1) 0.33
Fifth layer (intermediate layer)
                                          0.80
      Gelatin
      Anti-staining agent (HQ-2)
                                          0.03
                                         0.01
      Anti-staining agent (HQ-3)
      High boiling organic solvent (SO-2) 0.007
                                         0.04
      Anti-irradiation dye (AI-1)
4th layer (Red-photosensitive layer)
                                          0.90
      Gelatin
      Red-photosensitive emulsion (Em-R1) 0.27
                                          0.27
      Cyan coupler (EC-1)
      Anti-staining agent (HQ-1)
      Anti-foggants (AF-2 and AF-3 in equivalent moles)
                                           0.0002
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High boiling organic solvent (SO-1) 0.14

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Third layer (intermediate layer)
                                          0.80
      Gelatin
                                          0.03
      Anti-staining agent (HQ-2)
                                          0.01
      Anti-staining agent (HQ-3)
      High boiling organic solvent (SO-2) 0.01
Second layer (infrared-photosensitive layer)
                                          1.25
      Gelatin
      Infrared-photosensitive silver chlorobromide emulsion
                                          1.00
(Em-IR)
                                           0.50
      Yellow coupler (Y-1)
                                           0.20.
      Magenta coupler (M-1)
                                           0.35
      Cyan coupler (EC-1)
                                           0.04
      Anti-staining agent (HQ-1)
      High boiling organic solvent (SO-1) 2.00
      Anti-foggants (AF-1, AF-2 and AF-3 in equivalent moles)
                                           0.005
 First layer (anti-halation layer)
                                           1.20
       Gelatin
                                           0.055
       Anti-irradiation dye (AI-2)
 Thirteenth layer (reverse face layer)
                                           7.50
      Gelatin
                                           0.65
       Silica matting agent
       Structures of above-described compounds are as follows:
  [0175]
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SU-1: Sulfosuccinic acid di(2-ethylhexyl)ester sodium

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acid
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di(2,2,3,3,4,4,5,5-Octafluoropentyl) ester sodium

SU-3: Sodium tri-i-propyl naphthalene sulfonate

H-1: 2,4-dichloro-6-hydroxy-s-triazine sodium

H-2: Tetrakis(vinyl sulfonyl methyl)methane

SO-1: Trioctyl phosphine oxide

SO-2: Di-i-decyl phthalate

HQ-1: 2,5-di-t-butyl hydroquinone

HQ-2: 2,5-di(1,1-dimethyl-4-hexyloxycarbonyl butyl)

## hydroquinone

HQ-3: Mixture of 2,5-di-sec-dodecyl hydroquinone,

2,5-di-sec-tetradecyl

hydroquinone

and

2-sec-dodecyl-5-sec-tetradecyl hydroquinone (weight ratio: 1:1:2)

AF-1: 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene

AF-2: 1-(3-acetoamidophenyl)-5-mercaptotetrazole

AF-3: N-benzyl adenine

[0176]

[Chemical 31]

$$Y-1$$

#### Y-2

$$(CH_3)_3CCOCH_2CONH$$

$$O_5H_{11}(t)$$

$$O_5H_{11}(t)$$

$$O_5H_{11}(t)$$

#### M-1

### EC-1

$$\begin{array}{c|c} C_5H_{11}(t) & OH \\ \hline \\ C_5H_{11} & O-CHCONH \\ \hline \\ C_4H_8 & CI \\ \end{array}$$

# [0177]

[Chemical 32]

[0178]

Further, the sample Nos. 302 to 304 were prepared in a same manner as in the sample No. 301 except that dyes as shown in Table 3 were added in the first layer of the sample No. 301.

[0179]

The thus-obtained samples Nos. 301 to 304 were each allowed to be in contact with a cyan plate of small-dotted original exposing subjected to exposure under text and, then, condition-11 as described below. Next, the samples were allowed to be in contact with a magenta plate and, then, subjected to exposure under exposing condition-12 as described below. Thereafter, the samples were allowed to be in contact with a yellow plate and, then, subjected to exposure under exposing condition-13 as described below. Subsequently, the samples were allowed to be in contact with a mon ochromatic plate and, then, subjected to exposure under exposing condition -14 as described below. As for the small-dotted text, a text, having dots of 300 lines per inch, prepared by a screen method was used. Further, the number of dots per inch<sup>2</sup> at the time of a dotted area ratio of 40% was 90x103.

[0180]

<Exposing condition-11>

When each photosensitive material was exposed to white light through a red filter (Wratten No. 26) and an ND filter, the photosensitive material was exposed for 0.5 second with a minimum exposure amount which allows a red color density after development to appear lowest by controlling the ND filter density.

[0181]

<Exposing condition-12>

When each photosensitive material was exposed to white light through a green filter (Wratten No. 58) and an ND filter, the photosensitive material was exposed for 0.5 second with a minimum exposure amount which allows a green color density after development to appear lowest by controlling an ND filter density.

[0182]

<Exposing condition-13>

When each photosensitive material was exposed to white light through a blue filter (Wratten No. 47B) and an ND filter, the photosensitive material was exposed for 0.5 second with a minimum exposure amount which allows a blue color density after development to appear lowest by controlling an ND filter density.

[0183]

<Exposing condition-14>

When each photosensitive material was exposed to white light through an infrared transmitting filter and an ND filter, the photosensitive material was exposed for 0.5 second with a minimum exposure amount which allows a black color density after development to appear lowest by controlling an ND filter density.

[0184]

Further, as for a light source for each of the exposing

conditions-11 to 13, a daylight fluorescent lamp was used and, as for a light source of the exposing condition-14, a xenon lamp was used.

#### [0185]

Each sample which had been exposed was treated with treating condition-1 as described below, to thereby obtain a dye image made up of small dots. However, as for fogging exposure, the exposure was performed on an entire surface of the photosensitive material through a layer, having a thickness of 3 mm, of the developing solution in a state in which the photosensitive material was dipped in the developing solution.

[0186]

# <Treating condition-1>

| •     | Treating step           | Temperature |       | Time       |
|-------|-------------------------|-------------|-------|------------|
|       | Dipping                 | 37°C        |       | 12 seconds |
| •     | (developing solution)   |             | *     |            |
| ·     | Fogging exposure        | -           |       | 12 seconds |
|       | Development             | 37°C        | ;     | 95 seconds |
| ٠.    | Bleach-Fixing           | 35°C        | •     | 45 seconds |
|       | Stabilizing treatment   | 25 to 30°C  |       | 90 seconds |
| *     | Drying                  | 60 to 85°C  | ,     | 40 seconds |
| Color | forming development sol | ution:      | •     |            |
|       | Benzyl alcohol          |             | 15.0  | ml .       |
|       | Ceric sulfate           |             | 0.015 | g .        |
|       | Ethylene glycol         |             | 8.0 m | 1          |
|       |                         |             |       |            |

| Potassium sulfite                 | 2.5 g  |
|-----------------------------------|--------|
| Potassium bromide                 | 0.6 g  |
| Sodium chloride                   | 0.2 g  |
| Potassium carbonate               | 25.0 g |
| ST-1                              | 0.1 g  |
| Hydroxylamine sulfate             | 5.0 g  |
| Sodium diethylene triamine pentaa | cetate |
|                                   | 2.0 g  |

 $4-amino-3-methyl-N-ethyl-N-(\beta-methane \\$  sulfonamidoethyl)aniline 3/2 sulfate monohydrate

4.5 g

Fluorescent whitener (4,4'-diaminostilbene disulfonic acid derivative)

1.0 g

Potassium hydroxide 2.0 g

Diethylene glycol 15.0 ml

Water was added to make the total volume up to 1 liter and, then, a pH value was adjusted to be 10.15.
[0187]

Bleach-fixing solution composition:

Diethylenetriaminepentaacetic acid ferric ammonium salt

90.0 g

Diethylene triamine pentaacetic acid

3.0 g

Ammonium thiosulfate (aqueous 70% solution)

180.0 ml

Ammonium sulfite (aqueous 40% solution) 27.5 ml

3-mercapto-1,2,4-triazole 0.15 g

A pH value was adjusted to be 7.1 by using potassium carbonate or glacial acetic acid and, then, water was added to make the total volume up to 1 liter.

[0188]

Stabilizing solution composition:

O-phenyl phenol

0.3 g

Potassium sulfite (aquéous 50% solution)

12.0 ml

Ethylene glycol

10.0 g

1-hydroxyethylidene-1,1-diphophonic acid 2.5 g

Bismuth chloride

0.2 q

zinc sulfate heptahydrate

0.7 g

Ammonium hydroxide (aqueous 28% solution) 2.0 g

Polyvinyl pyrrolidone (K-17)

0.2 g

Fluorescent whitener (4,4'-diaminostilbene disulfonic acid derivative)

2.0 g

Water was added to make the total volume up to 1 liter and, then, a pH value was adjusted to be 7.5 by using ammonium hydroxideor sulfuric acid. Further, the stabilizing treatmen t was performed by a counter-current method of two bath constitution.

[0189]

In a small-dotted text in which the number of dots at

the time of the dotted area being 40% was 9x10<sup>3</sup>/inch<sup>2</sup>, in regard to an image obtained by treating with a fresh solution, quality of small dots present in such 40% area thereof was visually inspected by using a magnifying glass and relatively evaluated based on such a 5-point system as defining 5 as excellent and 1 as worst. The evaluation results are shown in Table 3.

[Table 3]..

| Sample No. | Dye of first layer (except Al-2) | Quality of small dot | Remark            |
|------------|----------------------------------|----------------------|-------------------|
| 301        | (except AI-2)                    | 3                    | Comparison        |
| 302        | 1-2                              | 5                    | Present invention |
| 303        | 1-16                             | 5                    | Present invention |
| 304        | 1-25                             | 4                    | Present invention |

[0191]

From these results, it is found that the quality of dots can be enhanced by using dyes according to the present invention.
[0192]

# Example 5

<< Preparation and Evaluation of Photothermographic Material>>

Comounds as shown below were dissolved in methyl ethyl ketone, to thereby prepare a colored composition solution. Next, the thus-prepared solution was applied on a polyethylene terephthalate film having a thickness of 100 µm and, then, dried,

to thereby prepare a colored transparent sheet. As for polyvinyl butyral, Butvar TMB76 manufactured by Monsanto Company was used.

[0193]

<Preparation of sample>

Polyvinyl butyral

 $0.85 \text{ g/m}^2$ 

Leuco dye (1)

 $1 \text{ mmol/m}^2$ 

Acid (1)

 $3 \text{ mmol/m}^2$ 

Dye (described in Table 4)

 $0.13 \text{ mg/m}^2$ 

[0194]

[Chemical 33]

Leuco dye (1)

Acid (1)

[0195]

<Exposing condition for forming image>

8 units of Spectra Diode Labs No. SDL-2430 (wavelength range: 800-830 nm) were combined to provide an image writing laser having an output of 800 mW. The laser was then adjusted

to give a laser beam having a diameter of 160 µm. The laser scanning speed was adjusted to 0.5 m/sec (center of scanning). The sample feed speed was adjusted to 15 mm/sec. The scanning pitch was adjusted to 8 lines/mm. Under these conditions, the foregoing samples were each subjected to exposure so as to form an image having a size of 22 mm x9 mm. The laser energy density on the sample was 10 mJ/mm². Further, by changing the laser scanning speed and the laser output, the energy density was changed as shown in Table 4.

[0196]

<Evaluation of color remaining ratio of laser scanning central
portion (image portion)>

A minimum density (Dmin) of a laser scanning central portion (image portion) is determined by measuring density of blue light or green light by Macbeth and, then, a color remaining ratio was evaluated based on a ratio between the thus-determined density and that in an unexposed portion. The results are shown in Table 4.

[0197]

[Table 4]

| Sample | Dye        | Dye remaini  | Dye remaining ratio (%) |            |  |
|--------|------------|--------------|-------------------------|------------|--|
| No.    |            | Laser energy | Laser energy            |            |  |
| ·      |            | density      | density                 | ·          |  |
| ļ      |            | 10 mj/mm²    | 5 mj/mm²                |            |  |
| 401    | Dye 2 for  | 15%          | 17%                     | Comparison |  |
|        | comparison |              |                         |            |  |
| 402    | 1-1        | 10           | 11                      | Present    |  |
|        |            |              |                         | invention  |  |
| 403    | 1-6        | 9            | 9                       | Present    |  |
|        |            |              |                         | invention  |  |

[0198]

[Chemical 34]

Dye 2 for comparison

[0199]

From Table 4, it has been found that the dye according to the present invention is small in the color remaining ratio.
[200]

Example 6

<<Pre>composition (Filter)>>

10 g of a dye as described in Table 5 was weighed out, added with 11.5 g of tricresyl phosphate which is a high boiling

organic solvent and, further, added with 24 ml of chloroform and, then, dissolved therein and, thereafter, the resultant solution was emulsify-dispersed in an aqueous 10% by weight gelatin solution containing 1.5 g of sodium dodecylbenzene sulfonate. An entire amount of such emulsify-dispersion was, after being added with an aqueous 10% by weight gelatin solution such that amounts as described below are allowed to be realized, applied on a support comprising a triacetyl cellulose film which has previously been provided with an undercoat layer and, then, layer, of thus-applied coating on 2,4-dichloro-6-hydroxy-s-triazine sodium was, after being added with an aqueous 10% by weight gelatin solution such that amounts as described below are allowed to be realized, applied as a protective layer, to thereby prepare samples 501 to 503. [0201]

## (1) Filter layer

Dyes as described in Table 5  $0.2 \text{ g/m}^2$ Tricresyl phosphate  $1.0 \text{ g/m}^2$ Gelatin  $3.8 \text{ g/m}^2$ 

# (2) Protective layer

2,4-dichloro-6-hydroxy-s-triazine sodium

 $0.1 \text{ g/m}^2$ 

Gelatin

 $1.8 \text{ g/m}^2$ 

Next, each sample was divided into two pieces and, then, one of these pieces was kept for 3 days at  $60\,^{\circ}\text{C}$  70% RH and the

other one was left for 2 days under an irradiation of 20000 lux of a fluorescent white lamp and, thereafter, densities of both pieces were measured. Percentages of the thus-measured densities relative to respective densities before such color fading test as described above were obtained, to thereby determine the remaining ratio of the dye. The results are shown in Table 5.

[0202]

[Table 5]

| Sample | Dye        | Remaining     | Remaining    | Remark     |
|--------|------------|---------------|--------------|------------|
| No.    |            | ratio (%)     | ratio (%)    |            |
| ·      |            | under forced  | under forced |            |
|        |            | conditions of | condition of |            |
|        |            | moisture and  | light        | *          |
|        |            | heat          | •            |            |
| 501    | Dye 2 for  | 80            | 82           | Comparison |
|        | comparison |               |              |            |
| 502    | 1-1        | 92            | 93           | Present    |
|        |            |               |              | invention  |
| 503    | 1-6        | 90            | 92           | Present    |
|        |            |               |              | invention  |

[0203]

From table 5, it is found that the compound according to the present invention is stable as a dye for the filter.
[0204]

[Advantage of the Invention]

According to the present invention, a recording material, a silver halide photographic photosensitive material, a photothermographic material and a thermally developable image

forming method which each contain a novel squarylium compound as a dye and, further, a thermally sensitive recording material containing the novel squarylium compound as a dye for thermal conversion and a thermally sensitive recording image forming method using the thermally sensitive recording material and, still further, an infrared ray absorbing composition containing the novel squarylium compound as a dye can be provided. Even still further, the novel squarylium compound can be provided.